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Behavior of DDT, Kepone, and Permethrin in Sediment-Water Systems under Different Oxidation-Reduction and pH Conditions

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BEHAVIOR OF DDT, KEPONE, AND PERMETHRIN IN SEDIMENT-WATER SYSTEMS UNDER DIFFERENT OXIDATION-REDUCTION AND pH CONDITIONS

by

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16. ABSTRACT

A study was conducted to determine the effects of pH and oxidation-reduction (redox) conditions of soil and sediment-water systems on the persistence of three insecticide compounds. Three pH levels, ranging from moderately acid to mildly alkaline, were studied for each compound. Four redox potential levels (-150, 50, 250, and 450 mv) were studied ranging from strongly reduced (anaerobic) to well oxidized (aerobic). The insecticide-substrate combinations included in the project were DDT in a Mobile Bay (Mobile AL) sediment material, Kepone in the sediment material of a tributary of the James River (Hopewell VA), and Permethrin in an Olivier soil material (Baton Rouge LA). Sample aliquots were removed from the laboratory microcosms to determine the recovery of the added compounds with time. A substantial redox potential effect was noted for DDT where recovery decreased from the spiking level of around 25 parts per million (ppm) to near 0 ppm within a few days at -150 mv (strongly reduced condition). A less rapid loss of DDT was noted at 50 mv (moderately reduced condition), but the pesticide appeared stable under better oxidized conditions during the 45-day incubations. The levels of Kepone recovered did not change appreciably during 56 days of incubation under any of the combinations of imposed pH and redox potential conditions. The recovery of Permethrin was affected by both pH and redox potential conditions over 25-day incubations. Unlike DDT, Permethrin was lost more rapidly under oxidizing conditions.

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FOREWORD

Environmental protection efforts are increasingly directed towards preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Systems Branch studies complexes of environmental processes that control the transport, transformation, degradation, and impact of pollutants or other materials in soil and water and assesses environmental factors that affect water quality.

Because of their widespread use in agriculture, synthetic organic pesticides have been the subject of considerable research to determine their their fate and transport in the environment, particularly in well-drained agricultural soils. Additional information is needed on the effects of physicochemical processes on pesticides in sediment systems where their residues have a potentially adverse effect. This report examines the effects of two important environmental parameters, redox potential and hydrogen ion activity, on the persistence of three pesticides in soil and sediment-water systems.

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ABSTRACT

A study was conducted to determine the effects of pH and oxidation-reduction conditions on the persistence of three insecticide compounds in soil and sediment-water systems. Continuously stirred suspensions spiked with the compounds were maintained at precise pH and redox potential levels for incubations of several weeks. Three suspension pH levels were studied ranging from moderately acid to weakly alkaline. Four redox potential levels studied ranged from strongly reduced (anaerobic) to well oxidized. Samples of the suspensions were removed periodically, extracted, and analyzed by gas chromatography to determine treatment effects on the concentration of the compounds with time. DDT, a chlorinated hydrocarbon, was studied in a Mobile Bay (Alabama) sediment material. Kepone, also a chlorinated hydrocarbon, was incubated with a sediment material collected from Bailey's Creek, a tributary of the James River, near Hopewell, Virginia. Permethrin, a chlorinated synthetic pyrethroid, was studied in an Olivier silty clay loam soil material from Baton Rouge, Louisiana.

The recovery of DDT decreased very rapidly under strongly reducing (-150 mv) conditions. This is consistent with information in the literature on DDT. The rate of loss decreased as redox potential increased. The two most commonly reported degradation products of DDT (DDD and DDE) were also measured. A moderate increase in DDD was noted early in the incubation of the strongly reduced treatment as DDT was rapidly being lost, but then DDD levels also declined rapidly after most of the DDT was removed.

There was little apparent effect of either pH or redox potential on the levels of Kepone added to the James River sediment material.

Both pH and redox potential affected the recovery of Permethrin. Unlike DDT, oxidizing conditions appeared to accelerate the loss of this compound from the soil system.

The results of this study suggest the physicochemical conditions of soil and sediment water systems should be considered in evaluating the potential environmental impact of organic pesticides. The persistence and fate of many of these compounds may differ depending on the environmental compartment in which

the compounds become associated and the physicochemical conditions of the various environmental compartments. For example, this study suggests Permethrin residues in typical upland agricultural soils may disappear much more quickly than residues which become associated with anaerobic sediments after being transported from a field by a runoff event.

This report was submitted in fulfillment of Grant No. 908940 by Louisiana State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 26 October 1976 to 25 July 1979, and work was completed as of 25 July 1979.

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SECTION 1

INTRODUCTION

Synthetic organic pesticides have been used extensively for almost three decades for controlling nuisance weed, insect, and microbial organisms. However, environmental problems sometimes arise when non-target organisms are adversely affected either as a direct result of pesticide application or waste disposal, or as a result of pesticide residues which may be transported to sensitive ecosystems away from the point of application.

Because of documented cases of environmental problems associated with synthetic organic pesticide use, pest control research has been directed to: 1) use of more selective and less persistent materials, 2) use of non-chemical means of pest control, 3) refinement of application equipment and methods, 4) improved monitoring of pest populations and activity in fields to permit more judicious scheduling of pesticide applications, and, 5) a combination of these procedures. Because of their effectiveness and economic benefits, it is likely that synthetic organic pesticides will continue to play a key role in most pest control programs for the foreseeable future.

A substantial amount of environmentally related research has been conducted with pesticides and especially insecticides such that much is known about their fate and mobility under certain environmental conditions. Most environmental studies on fate and transport have focused on well-drained agricultural soils. However, pesticide residues are subject to a wide range of physicochemical conditions in the environment. Soon after typical agricultural applications, most residues become associated with medium textured, well-oxidized, near neutral pH soils. Subsequently, these residues may be transported in dissolved or adsorbed forms to surface waters and sediments of streams, rivers, lakes, or estuaries where the physical and chemical properties (physicochemical) as well as biological populations of the receiving environment are very different from the conditions at the point of application. For example, typical agricultural soils exhibit a wide range in texture (from sandy to heavy clay material), pH commonly ranges from 5 to 7.5, soils are non-saline, and the organic carbon content of the plow layer typically ranges from a few tenths of a percent up to 2 percent. Compared to typical agricultural soils, sediments are characterized by finer texture (greater clay content), a narrower pH range (6.5 to 7.5), greater organic carbon content, moderate to strongly reducing (anoxic) conditions, and, depending on coastal proximity, sediments may have a higher salinity. These conditions have been shown to markedly affect the chemical mobility and biological availability of nutrients such as nitrogen and phosphorus, trace metals, toxic metals, petroleum hydrocarbons, and certain pesticides. For pesticides, these differences are thought to affect the adsorptive capacity of the solid phase for pesticides and the chemical and especially microbial processes affecting pesticide degradation.

There is sufficient published information available on pH and redox potential (oxidation-reduction conditions) effects on adsorption and degradation for selected pesticide compounds to document that these are important parameters to be considered in understanding the environmental fate of many pesticides. However, there is need for much more work to be done under carefully controlled pH and redox potential conditions to improve our understanding of factors affecting the environmental persistence and transport of pesticides. This is especially important since little is known of the physicochemical effects on the fate of most pesticide residues in some ecosystems, such as sediment-water systems, where residues have the greatest potential for biological accumulation and subsequent adverse effects. Such information should lead to development of improved predictive capability on the transport and fate of pesticide residues in various compartments of the environment.

This research was conducted to determine the effects of physicochemical conditions on the persistence of three pesticides in soil and sediment-water systems. Soil and sediment suspensions were incubated at selected pH and redox potential levels which include the range commonly found in these systems.

Three insecticides were studied. DDT [1, 1-bis-(p-chlorophenyl)-2, 2, 2-trichloroethane] was included because it is still widely distributed in the environment though its use has been eliminated or greatly restricted in recent years. Also, there is considerable published information for DDT on different degradative pathways and products dependent upon oxidation conditions. Additionally, since this was the first pesticide research conducted in this laboratory, it was desirable to use a compound for which much published information is available on extraction, cleanup, and analysis techniques. For example, it was believed that good and reproducible methods of sample preparation and extraction would be available from the literature such that these aspects of the study would present minimal problems and our attention could focus on the planned experimental parameters to be imposed on pesticide amended sediment-water systems. In practice, there were problems in most of the various procedural steps. An examination of the literature suggested this might be the case as there was considerable variability in the reported optimum preparation and extraction procedures for different soil and sediment materials. Also, most published DDT work has involved soil materials. The Mobile Bay sediment material used contains substantially more clay and organics than typical agricultural soils and can be expected to bind most synthetic organics more tightly. There was also a wide range of reported degradation times for DDT and its analogs. All of this suggested that the particular environmental materials studied play an important role in determining the suitability of the various reported procedures and the environmental fate determined from different studies. These points will be addressed in the following review of the literature.

Kepone [decachloro octahydro-1, 3, 4-metheno-2H-cyclobuta-[cd]pentalen-2-one] was included in these studies to determine if its persistence in the environment is influenced by physicochemical conditions. The known environmental problems with this compound are confined to the James River and connecting estuaries. Since essentially nothing was known of factors affecting Kepone persistence in soils and sediment-water systems, this compound was included to determine if studies of physicochemical effects on its persistence might suggest something about its fate in the James River and perhaps suggest management practices which can be used to minimize adverse environmental impacts.

The persistence of Permethrin, [3-phenoxybenzyl (±) _cis-trans_-3-(2, 2-dichlorovinyl)-2, 2-dimethylcyclopropanecarboxylate] a synthetic pyrethroid, was also studied under controlled physicochemical conditions. The synthetic pyrethroids are a relatively new class of insecticides which are highly effective against target insects, exhibit low mammaliam toxicity, and are far less persistent in the environment than many chlorinated hydrocarbon insectides. The high susceptibility of larvae and juvenile crustaceans to certain of these compounds and the expected increasingly important role of the synthetic pyrethroids in insect control programs suggest it is important to examine factors affecting the persistence of these residues in the environment.

Early in this work, it was apparent that published extraction procedures for recovering various pesticides from typical agricultural soils were often not effective when applied to typically fine textured, anaerobic sediments. Also, conventional drying of anaerobic soil and sediment materials containing relatively non-persistent pesticides which exhibit different degradative rates, depending on physicochemical conditions, was believed to introduce artifacts which affect results of degradation studies. A review of the literature revealed that almost all of the published extraction procedures involved agricultural soils. Thus an unplanned but important phase of this work was to develop and test sample processing procedures for fine textured anaerobic soils and sediments which give satisfactory and reproducible recoveries.

SECTION 2

CONCLUSIONS

A study was conducted to determine the effects of pH and oxidation-reduction conditions of soils and sediment-water systems on the persistence of three insecticide compounds. Soil or sediment materials amended with DDT, Kepone, and Permethrin were incubated as suspensions under conditions of carefully controlled pH and redox potential conditions in laboratory microcosms.

The effects of physicochemical parameters on the persistence and transformations of DDT were studied in a Mobile Bay sediment material at pH 6.0, 7.0, and 8.0. The recovery of DDT from the spiked Mobile Bay sediment material decreased very rapidly under strongly reduced conditions (-150 mV) such that 90 percent could not be recovered after as little as 5 days. This apparent rapid degradation rate under strongly reducing conditions was somewhat greater than reported in most published studies on the effects of reducing conditions on DDT persistence.

Several reasons for the rapid decrease in DDT recovery were considered. The "bound residue effect" (1) may be contributing to the low recovery of DDT early in the incubations. The extent of this process, if it is occurring, cannot be quantified, but it appeared unlikely this phenomenon was a major factor only at -150 mV. Artifacts introduced during sample processing (especially drying) were evaluated in the laboratory and eventually ruled out as a significant factor in the low initial recovery of DDT under strongly reducing conditions. Although the levels of known degradation products measured did not totally account for the loss in DDT, DDD levels were greatly increased where DDT was disappearing rapidly at -150 mV providing evidence that a substantial amount of DDT was actually degrading within a matter of 1 to 3 days. It was concluded that DDT was indeed degrading very rapidly under very strongly reduced conditions in the Mobile Bay sediment material compared to moderately reduced or oxidized conditions. It is probable the chemical properties and possibly the microbial activity of the strongly reduced Mobile Bay sediment material are very different from most soils and sediments used for DDT studies and that these differences contribute to very rapid losses of DDT from this material compared to most published degradation rates for DDT. Another factor may be that the -150 mV potential included

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in this study was a more intense reducing condition than is achieved in other studies of DDT degradation in flooded soils or soils equilibrated in the absence of air.

A less rapid loss was noted at 50 mV (moderately reduced conditions) while DDT appeared fairly stable under better oxidized conditions. Where recovery of DDT decreased rapidly (strongly reduced conditions), both DDD and DDE levels were elevated, but DDD predominated. Only at 50 mV was there an indication that a degradation product was accumulating in the Mobile Bay sediment material. The small increase in DDD levels noted with time was not equal to the rate of DDT loss indicating DDD was also not stable where conditions were conducive to rapid DDT degradation.

The results of these DDT studies were in general agreement with other published reports on the environmental fate of DDT with the possible exception that DDT degrades more rapidly under strongly reduced conditions in Mobile Bay sediment material than in most anaerobic soils and sediments.

The persistence of added Kepone was studied in James River sediment materials incubated at three pH (5.0, 7.0, and 8.0) levels and four redox potential levels (-150, 50, 250, and 450 mV). There was no clear indication that redox potential had any effect on Kepone recovery with time. Very gradual reduction in Kepone recovery was noted at all redox levels at pH 8.0 in the stirred suspensions.

The persistence of Permethrin, a synthetic pyrethroid, was studied in an Olivier soil suspension amended with this compound under a range of redox potential conditions at pH 5.5, 7.0, and 8.0. Both pH and redox potential strongly influenced the degradation of this compound. Unlike DDT, Permethrin was lost more rapidly under oxidizing conditions. Increasing pH enhanced this loss under both moderately reduced (+50 mV) and weakly oxidized (+250 mV) conditions.

The results of this study indicate Permethrin is more persistent under reducing conditions typical of sediments that are a habitat for many important benthic organisms which, according to the literature, are highly sensitive to some synthetic pyrethroids. Permethrin cannot be considered a persistent pesticide compound compared to most chlorinated hydrocarbons. However, its somewhat greater stability in reducing sediments which may receive residues in runoff, and the potential for adverse effects to organisms associated with sediment-water systems make physicochemical effects on Permethrin degradation an important environmental consideration.

The work with the three compounds included in this study demonstrated that pH and oxidation-reduction conditions do

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affect the persistence of pesticide compounds and that different compounds may respond differently to a given physicochemical environment. In this study, the stability of one compound was little affected by altered pH and oxidation conditions, another was markedly affected by oxidation conditions, and the degradation of the third was strongly influenced by both pH and redox potential conditions.

A substantial amount of environmentally related research has been conducted with pesticides and especially insecticides such that much is known about their fate and mobility under certain environmental conditions. Most environmental studies on fate and transport have focused on well-drained agricultural soils. However, pesticide residues are subject to a wide range of physicochemical conditions in the environment. Soon after typical agricultural applications, most residues become associated with medium textured, well-oxidized, near neutral pH soils. Subsequently, these residues may be transported in dissolved or adsorbed forms to surface waters and sediments of streams, rivers, lakes, or estuaries where the physical and chemical properties (physicochemical) as well as biological populations of the receiving environment are very different from the conditions at the point of application.

The ranges of physicochemical (pH and redox potential) parameters studied are commonly encountered in soils, sediments, and surface water which may receive pesticide residues. Also, temporary flooding of soils or certain dredged material disposal methods can alter the physicochemical properties of contaminated soils or sediments affecting the persistence and possibly the mobility of pesticide residues. Information on the effects of physicochemical conditions on the adsorption and degradation of specific pesticides should contribute to improved predictive capability on the transport and fate of pesticide residues in various compartments of the environment.

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SECTION 3

RECOMMENDATIONS

The results of this study demonstrated that the physicochemical conditions of the soil and sediment-water systems studied (pH and redox potential) substantially influenced the environmental chemistry of two of three synthetic organic pesticides included in this project. The results of this study and the very limited information available from the literature indicate that the persistence, degradation pathways and products, and the mobility of many or most synthetic organics may be affected by the physicochemical characteristics of the environmental compartments with which these residues become associated. Because of the apparent important effects of physicochemical conditions on the environmental chemistry of synthetic organics, and the wide range in these properties found in the various environmental compartments which may receive residues, it is important to understand the influence of physicochemical conditions on the environmental chemistry of pesticides before an accurate assessment can be made of the fate and potential impact of pesticide residues in all affected areas of the environment. For example, biometer flask studies of a compound such as Permethrin in a typical aerobic soil may not indicate the potential for persistence and accumulation in anaerobic lake and wetland sediment-water systems.

The following recommendations are made:

Because of probable physicochemical influences on the environmental chemistry of most pesticides, additional work should be done to characterize these effects for existing compounds where this information is lacking. Of particular importance are those compounds thought to be relatively persistent, compounds known to be especially toxic, particularly to non-target organisms, and compounds which are released into the environment in relatively large quantities. The non-volatile organics of the EPA priority pollutant list should be considered as prime candidates for studies of this type.

As part of the information the chemical industry is required to furnish when applying for registration to label and market a new pesticide product, testing should be done to determine persistence and pathways of degradation in soils and sediments under a range of physicochemical conditions. Also, the information should be obtained for a number of typical soils and sediments under their indigenous physicochemical conditions which should include a wide range of these properties.

Though the laboratory suspension studies of the type conducted in this project should accurately indicate the effects of physicochemical conditions on the environmental chemistry of the compounds studied, there is a need to systematically examine physicochemical effects under more natural conditions to more accurately reflect the rate of the processes under real world conditions.

The activity of microbial populations, either directly or indirectly, plays a major role in the fate of pesticide residues in the environment as well as in regulating the physicochemical conditions of the various environmental compartments. Thus studies should be done to characterize the relationship of the activity of microbial populations to the transformations observed for synthetic organics under various physicochemical conditions.

SECTION 4

LITERATURE REVIEW

A great deal of information has been published on the fate of DDT in the environment and on methods of extraction and analysis. There is considerably less information available on Kepone and the synthetic pyrethroids. The following review of literature will discuss these three classes of compounds individually.

DDT

DDT [1, 1-bis-(p-chlorophenyl)-2, 2, 2-trichloroethane] and certain of its analogs have been used extensively in many regions of the world for insect control beginning about 30 years ago. Studies which indicated the biological accumulation and environmental persistence of the DDT group of insecticides were the first to conclusively establish that the widespread use of certain synthetic pesticides can have serious environmental consequences. Because of its long-term use and environmental persistence, a substantial amount of information is available on the fate of DDT in the environment as well as information on methods of extraction and analysis.

DDT has been reported to volatilize rapidly from clean, moving water (2) with a half life of only a few days. In environmental water samples, the volatilization rate was decreased by a factor of 2- to 3-fold (still relatively fast), presumably due to the presence of suspended organic and inorganic particulates. Others have also reported rapid volatilization of chlorinated hydrocarbons from river water samples equilibrated in the absence of sediments, and essentially no volatilization into the atmosphere when water samples were associated with sediments (3). This is indicative of the strong partitioning of sparingly soluble, lipophilic chlorinated hydrocarbons with the solid phase of soil- and sediment-water systems. The effective scavenging of sediments for DDT group compounds is well established in the literature (4). Similarly, residues in soils are usually found in the surface horizons (5) and do not significantly leach into deeper soil layers and ground water. Organic matter content (6), and even the degree of humification of organic matter (7), the content of fine clays vs coarser material (8), the type of clay (9), and the presence of amorphous oxides of iron (6) are all thought to play important roles in adsorbing pesticides. Pionke and Chesters (6) suggested differences in structural composition of organics in reduced sediments vs. oxidized systems would likely contribute to greater adsorption by the reduced sediments in addition to the greater adsorption due to the usual greater organic matter content of reduced sediments relative to surrounding upland soils.

Although certain of the known degradation products of DDT have been used as the primary insecticide for some applications, p, p'-DDT is by far the predominant compound of the DDT group applied. More than a half dozen different degradation products of the parent compound have been identified (10, 11), but the primary degradation products reported in the literature are DDD [1, 1-bis-(p-chlorophenyl)-2, 2-dichloroethane] and DDE [1, 1-bis-(p-chlorophenyl)-2, 2-dichloroethylene]. It has been pointed out that commercially available p, p'-DDT applied contains some o, p-DDT, (12). Thus this compound and its degradation analogs have also been widely distributed in the environment, though in substantially lower concentrations than the p, p'-DDT group.

It is well known that the DDT group of compounds is very persistent in the environment with a "half-life" often reported in terms of years and even longer than a decade in many systems. However, there is a wide range in the reported persistence of DDT and surprisingly short degradation times for some systems have been reported. Some of the reported degradation times of DDT include: 4-10 years in unflooded soils, 60-180 days in flooded soils (review of literature by Sethunathan, [13]); about 20 percent at 30°C in 140 days in soils in the presence of water (14); 70 percent in 4 weeks in Crowley silt loam soil incubated under argon, and 80 percent with 1 percent glucose addition (Parr, Willis, and Smith, [15]); 50 percent loss of DDT in 24 hours in oxygen deficient lake waters (16); about 65 percent loss of DDT after 4 weeks in anaerobic soil (17); 20 percent in 7 days in flooded Raber silt loam at 30°C (18); 3 years in Oregon forest soils (19); and a half-life of 10 years in New Brunswick forest soils (20). Thus various published reports have indicated that the persistence of DDT may be more than 10 years in some natural systems and on the order of days for other systems. It is apparent from the wide range in reported DDT persistence in various natural systems that one or more environmental factors associated with soils and sediment-water systems must have marked direct and/or indirect effects on the degradation of DDT.

Influence of Environmental Physicochemical Parameters on the Fate of DDT

The degradation of DDT is temperature dependent. Gunzi and Beard (14) reported a loss of about 20 percent at 30°C and 50 percent at 50°C in 140 days in the presence of water. In another study, they reported a 20 percent removal in 7 days in a flooded Raber silt loam at 30°C and 35 percent in 7 days at 40°C (18).

DDD and DDE are thought to be the predominant initial degradation products of DDT in the environment and only a few investigators (11, 21) have attempted to look beyond DDT, DDD, and DDE when studying the environmental fate of the DDT group. Although DDD and DDE are thought to be lost from most systems, their degradation in soil has been very difficult to establish (12). It is widely reported that DDD is the major product of DDT degradation under anaerobic conditions and that DDE is the chief degradative product formed under aerobic conditions.

The DDE formed from the degradation of DDT in aerobic soil is resistant to further degradation (22). Metcalf et al. (23) compared the environmental behavior of DDT, DDD, and DDE in a model ecosystem. The DDE was found to be a highly persistent, lipid-partitioning metabolite of DDT which accumulated in animal tissues following the use of DDT. Their data also indicate that DDD is also a lipid-partitioning compound, however, it is more biodegradable than DDE. Toxicity of DDD is about one-tenth that of DDT (24).

Factors affecting DDT degradative processes include the amount and microbial availability of organic matter (energy source), temperature, pH, oxidation-reduction conditions, kinds and activity of microbial populations present, and certain other factors such as the presence of electron transfer substances like inorganic or organic iron forms. Many of these interacting factors are affected by oxidation-reduction conditions. Thus oxidation-reduction conditions should play a major role in the environmental fate of DDT and a review of the literature shows this to be the case.

Numerous investigators have shown that DDT is less persistent in anaerobic than aerobic soils (15, 21, 25, 26, 27) and that DDD is the principal degradation product in anaerobic or reduced soils and sediments while DDE is the principal degradation product in oxidized or aerobic systems (26). Farmer et al. (26) suggested DDE is the more hazardous of the two degradation products (as confirmed by reports of DDE accumulation in birds, certain mammals, and marine organisms), and it has been suggested that flooding should be considered where feasible as a management practice to encourage the DDD degradation pathway (26). Guenzie et al. (21) concluded that residues of DDT and other chlorinated hydrocarbon insecticides can be substantially reduced if the redox potential of field soils can be decreased to about 250 mV, a mildly reduced condition. Guenzi et al. (21) also state the available literature suggests that reduced soils and sediments result in different degradative microbial populations and breakdown pathways as well as differences in adsorption of pesticides to sediments and soils compared to oxidized or aerobic systems.

In a review of the literature, Sethunathan (13) reported studies indicating a 4- to 10-year persistence of DDT in unflooded soils while DDT disappeared from some flooded soils in 60 to 180 days. Although these data represent different studies and soil materials, they are indicative of the role of oxidation-reduction conditions in DDT degradation. Usually in soils with a readily available energy source, flooding is the general treatment used to obtain reducing or anaerobic conditions. It is interesting to note that Parr and Smith (15) noted a substantially greater loss of DDT in unamended and organic matter amended Crowley silt loam incubated under a nitrogen atmosphere at 1/3 bar moisture (approximate moisture content of a field soil following gravity drainage for 24 hours after saturation) than under flooded conditions. Even in soils incubated anaerobically, the degradation of DDT will occur more readily when the system is amended with an energy source. Of course, this enhances facultative and obligate anaerobic microbial activity and subsequently results in development of more strongly reduced conditions. Parr and Smith (15) found that although glucose amendments increased DDT loss from moist soil under a nitrogen atmosphere, alfalfa meal, rice straw, and rice hulls were much more effective.

In studies with Aerobacter aerogenes, Plimmer et al. (28), demonstrated the principal route of anaerobic microbial degradation was direct reductive dechlorination of DDT to DDD. They also suggested that a large number of facultative and obligate anaerobic bacteria can mediate this conversion under anaerobic conditions, but not aerobic conditions.

The formation of DDE from DDT can be due to biological or chemical dehydrochlorination, especially in alkaline environments. Guenzi and Beard (10) reported a comparison of DDE formation in sterile and nonsterile soil material revealed that 84 percent of the conversions was the result of chemical degradation at 30°C and the percentage was 91 at 60°C. In sterile soil material, the DDE formation rate was similar in submerged soil and soil with a 1/3 bar moisture content. The transformation of DDT to DDE was believed to be catalyzed by certain metals and minerals and they refer to studies where iron, iron chlorides, aluminum chlorides, and iron oxides catalyze the reaction at high temperatures (100°C to 130°C) in soils. Of course, natural soil and sediment temperatures would not approach these levels, but they point out that Lord (29) increased DDT degradation by adding ferrous sulfate, ferric ammonium alum, copper sulfate, and manganese sulfate to basic acetone solutions at 30°C. Again, an acetone solvent is not typical of soils and sediments, but a role of metals in catalyzing the degradation of DDT is suggested.

Guenzi and Beard (10) refer to the work of Nash (30) where conversion of DDT to DDE was very slow in a moist soil in the pH range of 4 to 6.8, but increased rapidly as pH increased from 6.8 to 7.5. It was suggested that the DDT conversion to DDE was principally a microbial process at lower pH, but probably a chemical process at higher pH levels. Many microbes are reported to possess the ability to transform DDT to DDE. The reaction is said to be catalyzed by iron, enhanced under alkaline conditions, and can be mediated by resistant insect strains (31).

Guenzi and Beard (10) concluded that conversion to DDE was mostly a chemical process with some microbial contribution in the systems studied. Water, temperature, and soil properties affect the conversion. They suggest from their studies and the literature that the transformation occurs at active sites which may be iron oxides. Others have cited studies suggesting that adding lime to increase pH, or adding aluminum or iron oxides to the soil materials studied failed to enhance the transformation of DDT to DDE and that microbial conversion is the predominant process in moist soil while chemical processes are most active in dry soils.

In a review of the literature, Sethunathan (13) cites work of Gunzie et al. suggesting DDD formation occurs at about the same redox potential at which nitrate becomes unstable in soils. References were cited giving evidence that once formed, DDD resisted further degradation. However, Castro and Yoshida (32) were reported to have found that DDD was removed faster from flooded than non-flooded soil, though the removal process was slower than DDT loss.

Others also reported from a review of the literature that DDD formed in flooded soils was more persistent than DDT and that DDD appears relatively stable in lake sediments (16). These people also cited studies in which 50 percent of the DDT in oxygen deficient lake water was transformed to DDD in 24 hours, certainly one of the fastest conversions reported for natural systems. Guenzi and Beard (10) reported that after 4 weeks of anaerobic incubation, 62 percent of the added DDT was in the DDD form and only 34 percent of the original DDT remained. Only traces of DDE were detected.

In a later study with a Raber silt loam material incubated with DDT under flooded conditions, 80 percent of the applied DDT was recovered unchanged after 7 days at 30°C, 12.3 percent as DDD, and 0.8 percent as DDE for a total recovery of about 93 percent. Although they cite studies where DDD accumulations account for the loss in DDT, in this study, they found a rapid degradation of DDT and a lack of an equivalent accumulation of DDD.

Glass (33) has suggested an irreversible redox reaction for the degradation of DDT under anaerobic conditions involving electron transfer from reduced organic materials through ferrous iron ions. The role attributed to soil microorganisms was in creating reducing conditions by depleting molecular oxygen followed by facultative and obligate anaerobic organisms using alternate electron acceptors (i.e., Fe^{3+}, Mn^{4+}, NO_3^-) to produce moderately to strongly reduced systems. The Fe^{+3} ion gains an electron from the metabolized organic substrate and becomes Fe^{+2} ion, an electron donor. The electron is then transferred to the DDT molecule which exhibits a strong electron affinity because of its chlorine atoms. In the process of electron capture, a chloride ion is released and the parent molecule exists as a free radical. This free radical abstracts a proton from a proton donor and forms DDD. Wedemeyer (34) reported that DDT dehydrochlorinated in the presence of reduced Fe(II)-cytochrome oxidase. The work of Ecobichon and Saschenbrecker (35) showed that the conversion of DDT to DDD would possibly result from the action of reduced coenzymes, porphyrins, and other metalloproteins from plant tissue and micro-organisms which probably degrade DDT by a chemical redox reaction rather than by an enzymatic reaction. Kearney et al. (31) suggested the microbial conversion of DDT to DDE is catalyzed by iron and enhanced with increasing pH conditions.

KEPONE

Kepone is a caged chlorinated hydrocarbon (C, 24.48%; Cl, 72.26%; and O, 3.26%) compound developed in the early 1950's and introduced as a pesticide by Allied Chemical in 1958. It is a white, crystalline, non-volatile solid reported to be insoluble in water. It is very stable as it is unaffected by strong acids and strong base (36).

It has been used as a fungicide and insecticide. It is reported to be highly effective against ants, roaches, as well as banana and potato insect pests, though its greatest use has been for banana pest control in Central America (37). Interest in the environmental impact of Kepone in the United States has centered on one incident in which a Kepone production facility discharged its toxic wastes through the Hopewell, Virginia sewage treatment plant resulting in Kepone contamination of the water, sediment, and biota of the James River as evidenced by traces of Kepone found in fish and shellfish from this area (38, 39).

Because Kepone has been demonstrated to be highly toxic and highly bioaccumulative to many aquatic and benthic organisms (40, 41), there is concern that a potentially serious Kepone threat to aquatic organisms and possibly human consumers may extend from the James River into the Chesapeake Bay. Because of the environmental persistence of Kepone, the occurrence or threat of adverse environmental impacts could continue for years.

Table 1 gives levels of Kepone found in selected compartments of the affected environment around Hopewell (42), and levels reported to cause specific adverse effects on selected species (41, 43).

TABLE 1. KEPONE LEVELS IN VARIOUS ENVIRONMENTAL COMPARTMENTS AROUND HOPEWELL, VIRGINIA, AND CRITICAL CONCENTRATIONS FOR SELECTED FISH SPECIES (41, 42, 43)

Environmental Compartment	Kepone Levels
James River water	0.1 to 4 ppb
fish and shellfish	0.1 to 20 ppm
Bailey's creek sediments	0.1 to 10 ppm most samples in the 1-4 ppm range
Hopewell sewage sludge	200-600 ppm
soil adjacent to Life Sciences (Kepone production) plant	10,000-20,000 ppm
soil 3000 ft. east of plant	2-6 ppm
96-hr LC_{50} for spot (*Leiostomus xanthurus*), most sensitive of several species treated (41)	6.6 ppb in water
Kepone concentration resulting in morphological effects on sheepshead minnows after 36 days exposure (43)	0.8 ppb in water

When this contamination event occurred, it was generally known that Kepone was a persistent compound in the environment, but relatively little was known about factors affecting its environmental persistence or its release from contaminated soils and sediments to more available forms. Various methods for cleaning up Kepone contamination have been studied, such as combustion (44), and in some cases implemented. In most cases, effective cleanup procedures have been limited to very localized situations such as disposal of waste from the production plant, adjacent waste disposal facilities, sewage treatment facilities, contaminated sludge, highly contaminated soils, and residences in the area. One EPA report even mentions plans are being developed and evaluated for dredging the James River (45). However, reports released later indicate cleanup of the contaminated James River by dredging "... may not be technically feasible or financially possible..." as dredging costs could approach $1 billion and require the equivalent of 120 dredging years to accomplish (46). Safe disposal of the contaminated dredged sediments would be substantial additional problems.

Although it is known or generally accepted that Kepone is very persistent in the environment, there has been little if any research on how various properties of soils or sediment-water systems may affect the degradation and mobility of Kepone. There is some evidence for degradation products of Kepone (36, 47), however, the identity of residual Kepone decomposition products in the environment have not been determined as far as we know.

Kepone was included in this study to determine if the physicochemical parameters of pH and oxidation-reduction conditions affect its environmental fate as has been found for many other pesticides. Although management practices based on physicochemical effects on the environmental fate of Kepone are not being contemplated at this time, it was anticipated studies of this type might provide some information useful for predicting the impact or persistence of Kepone contamination in certain environmental compartments.

PERMETHRIN

The development of resistance to conventional insecticides by the cotton bollworm (Heliothis zea Boddie) and the removal of remaining partially effective insectices such as DDT from general agricultural use has created a great deal of interest in the development of new insecticides that combine effective bollworm control with minimum adverse environmental effects. In England, recent developments in pyrethroid chemistry have resulted in the synthesis of relatively stable compounds with high toxicity to the cotton bollworm (48). This is a new class of compounds having great potential for insect control and is replacing the old class of natural pyrethrins which are manufactured from certain plant extracts. These synthetic pyrethroids are being used on an experimental basis and show such outstanding promise that there is little doubt they will be used throughout the Southern cotton growing areas if and when they receive final EPA clearance.

Natural pyrethins comprise the oldest class of organic insecticides known and have a long history of use. However, very little is known about the persistence or microbial degradation of natural or synthetic pyrethroids in soils (12).

The first class of synthetic pyrethroids which demonstrated characteristically high activity against insects and low mammalian toxicity as well as greatly increased stability were described by Elliott et al. (49, 50). These synthetic pyrethroids are more photostable than many of the common organophosphates and carbonates and are more insecticidally active by at least one order of magnitude. Many of these compounds were synthesized during 1973-1977. Because of their outstanding effectiveness against many insects, these compounds will likely be introduced commercially to replace or compliment many existing products used for a variety of insect pests.

Synthetic pyrethroids include: 1) Allethrin; 2) Bioallethrin; 3) S-bioallethrin; 4) Tetramethrin; 5) Resmethrin; 6) Bioresmethrin; 7) Cismethrin; 8) Phenothrin; 9) Permethrin; 10) Cypermethrin, and 11) Fenvalerate. Various other synthetic pyrethroids which have been tested but which have not been designated by common names include: 1) FMC 33297 (3-phenoxybenzyl (±)-3-(2, 2-dichlorovinyl)-2-2-dimethylcyclopropane carboxylāte); 2) Shell WL 41706 (α-cyano-3-phenoxybenzyl-2, 2, 3, 3-tetramethylcyclo-propane carboxylate); 3) Shell WL 43775 (α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-3-methyl-1-butyrate); 4) RU 11679; 5) RU 15525, and others (51, 52).

All these synthetic pyrethroids are lipophilic compounds, almost insoluble in water. In these respects they resemble the chlorinated hydrocarbons. They are high boiling viscous liquids and most exhibit low vapour pressure (53).

These pyrethroids were found to be 3 to 8 times more toxic to fish and insects at low temperature (15°C) compared to high temperature (32°C) (51, 54). No other work has been reported on the kinetics of their degradation under various temperature regimes.

Very little has been reported on the behavior of pyrethroids in soil. Their physical properties would suggest relatively low mobility in soil. Their low vapour pressure suggests that their vapour diffusion in soil air space will not be significant (55). Their highly lipophilic character with octanol-water coefficients greater than 10^5 (56) suggests that synthetic pyrethroids would be strongly adsorbed in most soils and thus not leached readily from the point of application or deposition (57). Significant amounts of these compounds are likely to enter surface waters only by direct application or by sediment transport from treated soils and not by diffusion or leaching.

Very little is known of the metabolism of pyrethroids in soil. Kaufman et al. (58) recently reported that Permethrin is extensively degraded by soil microorganisms within 4 weeks by ester cleavage and oxidation, eventually to carbon dioxide. Pyrethroid esters with α-cyano groups have been reported to be relatively more stable (59).

To date, work on the behavior of some of these synthetic pyrethroids in soils has been reported only by Roberts and Standen (60). They studied the degradation of cypermethrin and geometric isomers of NRDC 160(cis-) and NRDC 159(trans-) in three soils varying in texture. The rate of degradation was most rapid on sandy clay and sandy loam soils compared to a fine textured soil. The major degradation route in all soils was hydrolysis of the ester linkage leading to formation of 3-phenoxybenzoic acid and 3-(2, 2-dichlorovinyl)-2, 2-dimethylcyclopropane carboxylic acid. A minor degradative route was ring-hydroxylation to give an α-cyano-3-(4-hydroxyphenoxy) benzyl ester, followed by hydrolysis of the ester bond. Under waterlogged conditions, the rate of hydrolysis of cypermethrin on sandy loam soil was slower than under aerobic conditions, and 3-phenoxybenzoic acid accumulated in the anaerobic soil. This finding suggests the possibility of greater buildup of synthetic pyrethroids in wetlands than in upland soils. Their study indicates that oxidation-reduction conditions (redox potential) of soil systems have a major effect on the degradation of synthetic pyrethroids. Because redox potential and pH are inversely related in many soils, and because ester hydrolysis reactions are influenced by the degree of acidity or alkalinity, pH should also have an effect on the degradation of pyrethroids.

Synthetic pyrethroids have been reputed to be very toxic to fish. The lipophilic nature of these pyrethroids indicates that they will be strongly absorbed/adsorbed by the gills of fish even from very low concentrations in water. Mauck et al. (54) reported toxicity of natural pyrethrins and synthetic pyrethroids to fish. Miyamoto (61) gave preliminary data on the toxicity of optical and geometrical isomers of phenothrin, permethrin, resmethrin, and tetramethrin. Their data indicate that pyrethroids were far more toxic to killifish than organophosphates and carbonates (62).

Jolly et al. (63) reported the acute toxicity of a pyrethroid (Pounce) to aquatic animals. Results of their study are given in Table 2. Crawfish were most sensitive to Pounce since they are phylogenetically close to insects. Even a concentration of less than half of one part per billion killed more than 50% of the population in 96 hours. The high degree of toxicity of Pounce to crawfish is in the same range as most toxic organochlorine insecticides such as DDT, Endrin, and Toxaphene. Pounce is now being used in limited quantities under an experimental label.

TABLE 2. TOXICITY OF POUNCE TO SEVERAL AQUATIC ANIMALS (JOLLY ET AL., 1978).

Species	Mean weight (grams)	Total length (millimeters)	Concentration (ppb) required to kill 50% in 96 hours
Crawfish, newly hatched	0.05	8-12	0.39
Crawfish, juvenile	0.50	20-30	0.62
Channel catfish	0.02	14-17	1.10
Bass	1.14	45-55	8.50
Mosquitofish	0.25	15-25	15.00
Bullfrog tadpoles	0.01	6-8	7,033.00

In Louisiana and other coastal states in the United States, much of the land used for agriculture is in close proximity to lakes, streams and ponds that support aquatic animal populations which are of great commercial importance. The transport and persistence of pyrethroids in sediment-water systems are of particular concern because of the demonstrated toxicity to some benthic species. Benthic species potentially affected may be commercially important species or lower members of predominantely aquatic food chains. The crawfish industry is very important to Louisiana and other coastal states. In Louisiana, the annual value of pond-raised crawfish has been estimated to be $10 million.

SECTION 5

MATERIALS AND METHODS

EXPERIMENTAL MICROCOSMS

Pesticide-amended soil and sediment suspensions were incubated under controlled pH and redox potential conditions using the microcosm shown in Figure 1. Suspensions were maintained in the 2-liter, 3-necked, flat-bottomed flasks by continuous stirring of the soil- or sediment-water mixture using a motor-driven magnetic stirrer. Flexible polyvinyl chloride (Tygon) tubing was placed over the 2-inch (5.08 cm) teflon-coated magnetic stirring bar in the flask to prevent abrasive wear to the stirring bar. Each flask was equipped with a combination pH electrode for measuring pH, two platinum electrodes for monitoring redox potential, a thermometer, a serum cap for adjusting pH or extracting samples, separate inlet tubes for air and nitrogen, and an outlet tube, the end of which was submerged in a water trap to prevent gaseous oxygen diffusion into the flask.

All suspensions were maintained at 28°C ± 1°. Thin cardboard or asbestos sheets were placed between the flask and the stirring motor as required to control heat transfer from the stirrer motor.

The two bright platinum electrodes positioned in the sediment suspension were connected to a millivolt/pH meter (Beckman Zeromatic, SS-3) for redox potential monitoring and control. A saturated calomel reference electrode was connected to the suspension with a saturated potassium chloride-agar salt bridge. This laboratory-made reference electrode system was more satisfactory than a commercial calomel reference electrode since our experience has shown the solution contact (junction) on many reference electrodes tend to clog with time when immersed in highly colloidal materials. This contributed to excessive junction potentials resulting in error to the redox potential measurement. The recorder output of the millivolt/pH meter was connected to a meter relay (General Electric Type 196) which switched on an aquarium-type air pump whenever the redox potential dropped below the preset level for each incubation flask. Slow oxidation of the suspension during the aeration

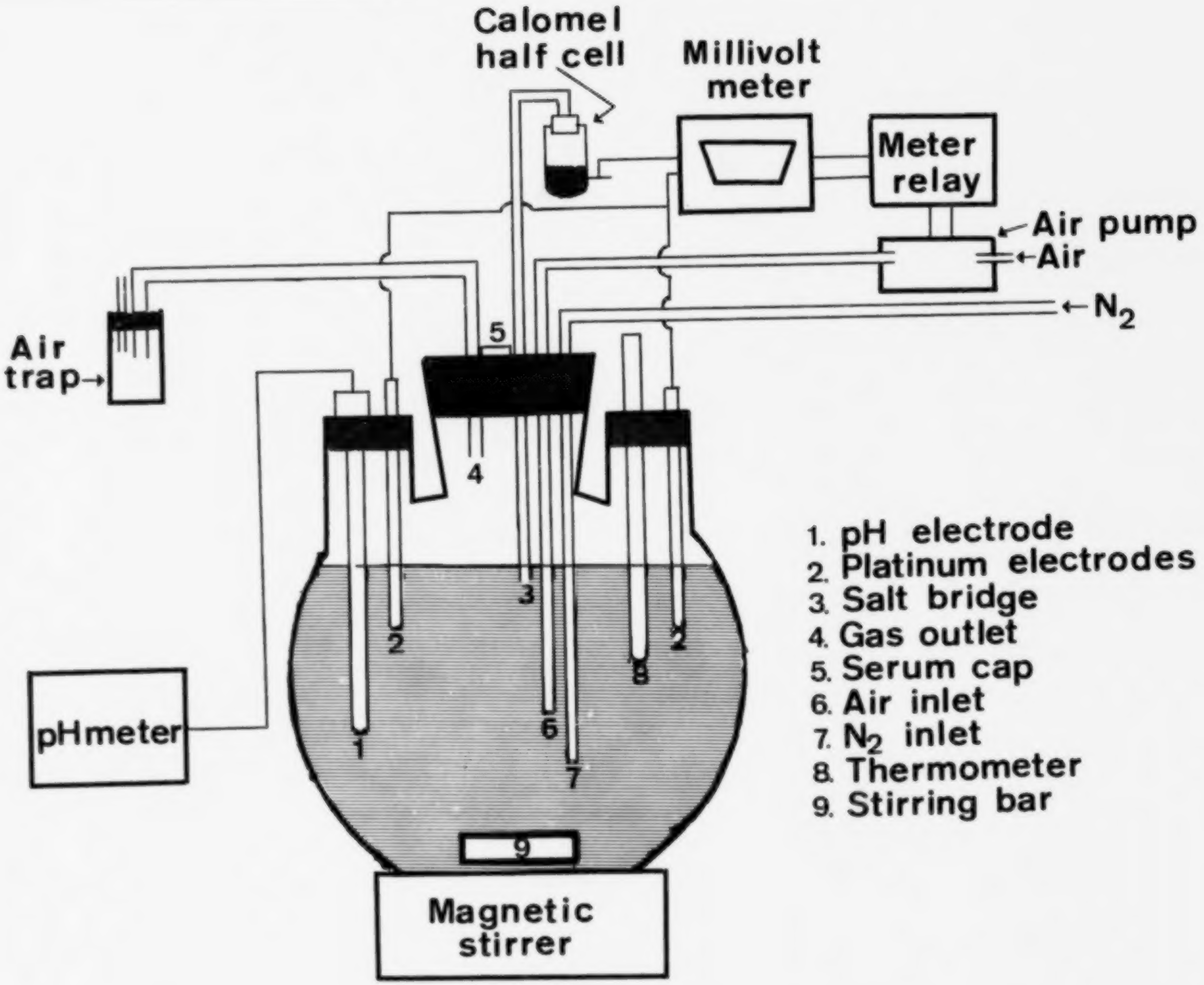
Calomel half cell
Millivolt meter
Meter relay
Air pump
←Air
←N_2
Air trap→
pHmeter
Magnetic stirrer
1
2
3
4
5
6
7
8
9
1. pH electrode
2. Platinum electrodes
3. Salt bridge
4. Gas outlet
5. Serum cap
6. Air inlet
7. N_2 inlet
8. Thermometer
9. Stirring bar

Figure 1. pH and Redox Potential Control Apparatus for Incubating Pesticide-Amended Soil and Sediment Suspensions.

cycle was achieved by metering the air flow to about 1 to 4 ml/minute. When the redox potential again reached the preset potential, the meter relay would automatically switch off the air pump.

Oxygen-free nitrogen gas was continuously supplied to the suspension at a rate of about 5 ml/minute through a separate gas inlet. This nitrogen gas was effective in: 1) removing air contamination from possible small leaks in the system, 2) preventing an accumulation of gaseous decomposition products such as carbon dioxide or possibly hydrogen sulfide which might affect microbial activity, and, 3) purging excess oxygen from the system at the end of the aeration cycle.

In the absence of oxygen, soils and sediments with sufficient organic matter content to support appreciable microbial activity tend to become more reducing. Thus the oxidation-reduction levels of a soil or sediment water system can be controlled over a wide redox potential range by regulating the addition of air to the system. Using the microcosms as described above permits redox potential control to within 5 to 10 millivolts of the desired potential.

Suspension pH was checked once or twice daily and adjusted to the proper level as required using a syringe to add 1N hydrochloric acid or 1N sodium hydroxide through the serum cap located in the center rubber stopper. The combination pH/reference electrodes used (Beckman Model 39504) required infrequent recalibration since the reference electrode portion, equipped with an annular ceramic reference junction, was less affected by a gradual changing junction potential due to clogging by colloidal particulates.

All soil and sediment materials were batched when initially received and then separated into smaller glass or plastic-lined metal containers for storage at 4°C in their natural moist or saturated conditions until needed in laboratory incubation studies. Each small storage container was thoroughly mixed on a roller-mixer immediately prior to weighing out into the incubation flasks. Sufficient water was added to adjust the solids to solution ratio to the desired level (300 grams soil or sediment solids, on an oven dry basis, plus 1500 grams of water), and stirring was then begun for the preliminary incubation. The preliminary incubation consisted of gradually adjusting both pH and redox potential conditions of the suspension in each vessel to preselected levels. Stored soil materials required this preincubation to obtain reducing conditions while sediments had to be oxidized from their initially reduced condition. Thus before pesticide amendments, all of the four suspensions had achieved preselected redox potential levels ranging from strongly reduced to well oxidized. Seven to 10 days were usually required to achieve all of the preselected redox potential levels and this was followed by an additional 4 to 7 day equilibration at the treatment pH and redox potential levels before the suspensions were amended with pesticides.

Samples were obtained from the flasks by withdrawing suspension aliquots from the incubation flasks using a 50- ml glass syringe equipped with a 12 gauge, stainless steel needle. The sample aliquots were placed in 4 oz (112 ml) glass bottles for further processing. If the samples were to be stored before extraction, an aluminum foil-lined cap was fitted on the glass bottle and the sample placed in a freezer until needed for extraction and analysis.

DEGRADATION STUDIES

DDT

Sediment Material--
For all studies with DDT, Mobile Bay sediment material was used. The sampling site was about 800 meters east of the Mobile Bay ship channel near buoy #38. This was approximately 8 to 9 km south of the main harbor area of Mobile, Alabama. Sediments were collected with a Peterson dredge lowered by rope where the water depth at the time of sampling was 2.5 to 3 meters. The sediment material as collected was strongly reduced (-160 mv) and at pH 7.3. It had an organic carbon content of 1.8 percent and a clay (less than 2 μ) content of 44 percent. All of the sediment material was batched, thoroughly mixed, then stored in 1 gallon amber glass bottles under a N_2 atmosphere at 4°C until needed.

Amending Sediment Suspensions--
Mobile Bay sediment suspensions which had been equilibrated for about a week after reaching the planned pH and redox potential conditions were slowly amended with reagent grade DDT dissolved in about 10 ml acetone at levels of 25 or 40 μg/g sediments on an oven-dry solids basis. Since DDT is soluble in acetone, it was anticipated the acetone carrier would quickly distribute the DDT evenly through the suspension after which the carrier should either volatilize or be readily degraded and quickly removed from the system. The spiking level for individual experiments was: pH 6.0, 25 μg/g; pH 7.0, 40 μg/g; pH 8.0, 25 μg/g.

DDT Extraction and Analysis--
In the laboratory studies of DDT degradation in sediment suspensions, it was anticipated that DDT, DDD and DDE would be strongly partitioned with the solid phase such that dissolved levels in the aqueous phase would be negligible in terms of total DDT's present. This hypothesis was investigated and

confirmed by extracting the aqueous phases of a spiked sediment-water suspension and measuring the solution phase DDT. This amount was negligible compared to DDT levels extracted from the sediment phase. Thus in our laboratory studies, physicochemical effects on degradation could be determined by considering the change in DDT levels associated with the solid or sediment phase. Therefore, the solution phase was separated by centrifugation and discarded and only the solid phase was extracted for DDT, DDD and DDE.

The following procedure was used to extract DDT, DDD and DDE from reduced sediment-water suspension samples in this study. Background information on the use of this procedure is presented under the heading of Development and Testing of Procedures (page 72). Oxidized samples were processed similarly except that after centrifugation, the sediment material was dried in a forced draft oven at 35°C.

DDT extraction steps--1. Thaw sample. 2. Centrifuge thawed sediment-water mixture in the glass storage bottle at approximately 1,000 RCF for 15 minutes. An 0.5 g NaCl amendment was mixed into the sample to enhance flocculation of solids during the centrifugation step where necessary. The resulting aqueous supernatant phase was clear. 3. Discard water phase. 4. Add 15 ml acetone, cover with aluminum foil, and seal bottle with screw cap. 5. Use shaker for 2 minutes to disperse sediment phase in acetone. 6. Centrifuge at about 1,000 RCF for 10 minutes. 7. Decant acetone layer and save as this contains some DDT. 8. Repeat steps 4-7 using a new aluminum foil cover. 9. Evaporate acetone residue in sediment under a stream of compressed nitrogen for about an hour. 10. Grind sediment to a fine powder using porcelain mortar and pestle. 11. Weigh and label Soxhlet extraction thimbles, weigh into thimbles 3-5 grams of the dry, ground sediment and determine the exact sample weight. 12. Place thimble into a clean and dry Soxhlet extraction apparatus, connect to a boiling flask containing 3 to 5 glass beads and 130 ml of a 3:1 hexane:acetone mixture and 1 ml of 0.01 percent Nujol solution in hexane. Attach condenser to top of Soxhlet apparatus. Be sure all joints are tight. A drop or two of Nujol will seal the occasional ground glass joint connections found to have slow leaks. 13. Extract for 12 hours with individual heating elements adjusted for about 6 cycles per hour. 14. After extraction is complete, siphon over as much solvent into the boiling flask as possible by tipping extractor. 15. Place the thimble in a glass funnel in top of Soxhlet extractor and let thimble drain completely. Rinse thimble and funnel with acetone. 16. Siphon over the remaining solvent and acetone rinse into the boiling flask and rinse extractor twice with acetone. 17. Pour the solvent/pesticide mixture through a funnel equipped with a glass bead trap into a clean 250 ml separatory funnel. Rinse the boiling flask and bead-trap funnel with acetone into the separatory funnel. 18. Add the acetone rinses from the sediment drying steps into the separatory funnel. 19. Add 50 ml of NaCl-saturated water to the separatory funnel, shake for two minutes venting often, and permit layers to separate. 20. Drain off the bottom water layer (the salt prevents an emulsion from forming and the water removes the acetone which should not be run through an electron capture detector). 21. Add 50 ml of distilled water, shake for 2 minutes venting often, let separate, then drain off excess water. 22. Repeat step 21 twice more. Separation of aqueous phase may require more time after each addition of water. 23. Set up a clean 200 ml volumetric flask to receive the eluant from a filter funnel filled with sodium sulfate washed with hexane for each sample. 24. Pour contents of separatory funnel through the sodium sulfate and rinse separatory funnel and sodium sulfate funnel twice with hexane. 25. Make 200 ml volumetric to volume with hexane and mix well. This is the "concentrated" sample. 26. Where dilution was necessary, 2 ml of the "concentrated" sample was made to volume with hexane in a 25 ml calibrated, screw-capped test tube and mixed. 27. For some reduced samples where sulfur caused problems with the GC analysis, a 12 gauge copper wire pretreated with $4\underline{N}$ HNO_3 was added to the sample tube to remove this interference. 28. Inject 5 µℓ of sample into the gas chromatograph.

DDT, DDD, and DDE were analyzed on a Perkin-Elmer Model 3920 B gas chromatograph equipped with a Ni-63 electron capture detector, P-E Model 023 dual pen recorder, and a P-E Model M-1 Intergrator. Typical instrument operating parameters are given below for DDT.

Column: glass, 6 foot length, 1/4-inch diameter, 10 percent OV-1 on Chromosorb W, 80/100 mesh
Flow Rate: 70 ml/minute
Carrier Gas: Zero grade nitrogen (Matheson)
Injector Temperature: 240°C
Column Temperature: 220°C
Interface Temperature: 250°C
Detector Temperature: 275°C

DDT, DDD, and DDE standard materials were Analytical Reference Standards obtained from the Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Sample concentration was determined by comparing sample peak height with standard peak height (considering signal attenuation differences) or by comparing peak areas of samples and standards when the intergrator was used. With the instrumentation described, it was determined the signal was linear with changes in concentration up to and including an attenuation setting of 512. Samples which went off the recorder chart at an attenuation of 512 were diluted and run again. This linear range was also found to apply to Kepone and Permethrin as well.

Kepone

Sediment Material--

Studies of Kepone persistence under controlled physicochemical conditions were conducted using a sediment material taken from a mud flat/marsh grass area adjacent to Bailey's Creek near Hopewell, Virginia. This is part of the area affected by Kepone contamination from the Life Science Kepone manufacturing plant located in Hopewell. Although not inundated at the time samples were obtained, it was apparent the sampling area adjacent to Bailey's Creek was subject to periodic flooding and that the sample material was deposited by sedimentation.

Sediment samples were shoveled into plastic-lined, 5-gallon paint buckets, sealed, and shipped to Baton Rouge by commercial bus. This material was moist, but not water saturated. In the lab, the sediment material was composited, spread thinly, and large pieces of roots and other undecomposed plant material removed by hand. The composited samples were mixed and returned to the original 5-gallon container and stored in a moist condition at 4°C until used in incubation studies. This material contained approximately 2 μg/g Kepone as collected and is designated as James River sediment material elsewhere in this report.

Amending Sediment Suspensions--

James River sediment material which was incubated as a suspension at selected pH and redox potential conditions was amended with a solid Kepone spiking material. This material was prepared by grinding 37.5 mg of Kepone (99% purity, pesticide standard grade material from Applied Science Laboratories, Inc.) with 30 grams of a silty loam soil which had been combusted at 900°C to destroy organic matter. Five grams of this Kepone-amended soil material containing 6.25 mg Kepone was added to each suspension (containing 300 g sediment solids) as an aqueous slurry (20 ml H_2O) to give a spiking level of about 21 μg/g.

Kepone Extraction and Analysis--

As described for the DDT studies, it was determined that essentially all of the Kepone in the incubated suspensions was associated with the solid phase. Therefore, the aqueous sample phase was separated and discarded.

Although apparent degradation products of Kepone have recently been observed on gas chromatograms (47), during the time of this study, the identity of possible Kepone degradation products was unknown and thus no standards were available for identification and quantification of degradation products (36).

Thus this study looked only at levels of Kepone vs. time in the controlled incubations as a measure of physicochemical effects on the persistence of Kepone.

The following procedure was used to extract Kepone from the sediment-water samples for the Kepone data reported in this study.

Kepone extraction steps--1. Thaw sample. 2. Add 0.5 grams of NaCl and mix with sample to enhance flocculation of solids during centrifugation. 3. Centrifuge the sediment-water mixture in the glass storage bottle at approximately 1,800 RCF for 45 minutes and discard the water layer. 4. Add 15 ml of acetone, then seal the bottle with an aluminum foil-lined screw cap. 5. Disperse sediment-acetone mixture for 2 minutes on a mechanical shaker. 6. Centrifuge at approximately 1,800 RCF for 15 minutes, decant, and save the acetone extract as it contains some Kepone. 7. Repeat steps 4-6 using a new aluminum foil liner if necessary. 8. Dry the sediment (evaporate the acetone) under a stream of compressed nitrogen for about 1 hour. 9. Grind the sediment material to a fine powder. 10. Label and weigh Soxhlet extraction thimbles, weigh into labelled thimbles 3-5 grams of the dry, ground sediment material, and determine exact sediment weight. 11. Place thimbles into a clean, dry Soxhlet extraction apparatus, connect to a boiling flask containing several glass beads and 130 ml of a 1:1 benzene-methanol mixture, and attach condenser to top of Soxhlet apparatus. Be sure all ground glass connections are tight. 12. Extract for 12 hours with heating units adjusted for about 6 cycles per hour. 13. After extraction is complete, siphon over as much solvent into the boiling flask as possible by tipping extractor. 14. Place the thimble in a glass funnel positioned in the top of the Soxhlet extractor and let the thimble drain completely. Rinse thimble and funnel with acetone. 15. Siphon over the remaining solvent and acetone rinse into the boiling flask and rinse extractor twice with acetone. 16. Pour the solvent/pesticide mixture through a funnel equipped with a glass bead trap into a clean 250 ml separatory funnel. Rinse the boiling flask and bead trap funnel with acetone into the separatory funnel. 17. Add the acetone rinses from the sediment drying steps into the separatory funnel. 18. Add 50 ml of NaCl-saturated water to the separatory funnel, shake for two minutes venting often, and permit the layers to separate. 19. Drain off the bottom water layer. 20. Add 50 ml of distilled water, shake for 2 minutes venting often, let layers separate, then drain off the excess water. 21. Repeat step 20 twice more. 22. Set up a clean 250 ml volumetric flask with a filter funnel filled with sodium sulfate for each sample. 23. Dilute as necessary to bring concentration within linear range of the gas chromatograph's electron capture detector.

Kepone was analyzed on the same gas chromatograph with the same operating paramters as described for DDT except that a 6-foot glass column with a 1/4-inch diameter packed with 1.5 percent OV-1, 1.95 percent QF-1 on 80/100 mesh Chromosorb W was used.

Kepone standard material was Analytical Reference Standards obtained from the Health Effects Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. Kepone standards were made in a 95 percent benzene, 5 percent methanol solution.

Permethrin

Soil Material--

The effects of controlled pH and oxidation-reduction conditions on the degradation of Permethrin were studied using aqueous suspensions of an Olivier silty clay loam soil obtained from the Louisiana State University Agricultural Experiment Station Burden Research Center in Baton Rouge. The soil material was obtained at field moisture conditions, air dried, ground, and stored in a dry state at ambient temperatures until needed for pesticide degradation studies.

Amending Soil Suspensions--

Aqueous suspensions of the Olivier soil material were amended with Permethrin dissolved in acetone. The Permethrin material for the controlled pH-redox potential studies was obtained from Applied Science Laboratories. The pesticide material for a preliminary Permethrin study was obtained from Dr. Sammy Smith of the USDA Soil and Water Pollution Laboratory, Baton Rouge, Louisiana, who had research material from the FMC Corporation, developer of the compound. The purity of the FMC Corporation material was reported to be 94.5 percent. The compound was reported to consist of cis and trans isomers comprising 38.8 and 61.2 percent of the total material respectively. The soil suspensions were amended with Permethrin dissolved in acetone. The initial spiking level was 15 to 17 µg/g oven dry soil solids.

Permethrin Extraction and Analysis--

The procedure which gave the best and most reproducible recovery for our experimental materials were similar to those described previously for DDT with the following exceptions:

A 60:40 hexane:acetone solution was used with an 8-hour Soxhlet extraction. The GC oven temperature was 200°C, and a 6-foot, 1/4-inch diameter glass column packed with 5 percent SP-2330 on Chromosorb W was used. This column permits separation of the cis and trans isomers.

A preliminary study was conducted with Permethrin at two pH levels (5.5 and 7.5) under conditions of continuous nitrogen purging (to simulate anaerobic or reducing conditions) and continuous air purging (to simulate aerobic or oxidizing soil conditions).

SECTION 6

RESULTS AND DISCUSSION

DDT

DDT-amended Mobile Bay sediment material was incubated at three pH levels ranging from mildly acid to mildly alkaline (6.0, 7.0, and 8.0) and four redox potential levels ranging from strongly reduced to well oxidized (-150, 50, 250, and 450 mv) to determine the effects of these physicochemical conditions on the levels of DDT and its two predominate degradation products, DDD and DDE, with time. The effects of pH on recovery of DDT from the amended sediment material were negligible at each of the four redox potential levels studied. However, redox potential treatments greatly affected the recovery of DDT.

Under well oxidized and weakly oxidized (+450 and +250 mv) conditions for all three pH levels studied, the recovery of DDT decreased to about two thirds of initial levels during the first two weeks of the incubation (Figures 2-4). After two weeks until the end of the incubations at about 45 days, DDT recovery remained essentially unchanged or perhaps decreased slightly.

DDT recovery decreased at a gradual and almost uniform rate during the entire incubation under moderately reduced (+50 mv) conditions such that only about one-third of the initial levels was recovered at pH 6.0 and 7.0 and about one-fourth initial levels recovered at pH 8.0 after 45 days.

Under strongly reducing conditions (-150 mv), DDT recovery decreased to about 10 percent of spiking levels within 2 to 5 days after which recovery approached zero for the duration of the incubation.

Although numerous studies have reported more rapid degradation of DDT under reducing soil conditions compared to well-drained, oxidized soils, this apparent rapid degradation (greater than 90 percent in a few days) at -150 mv warrents additional discussion. We were able to find only one other published report of comparable DDT degradation rates in the literature, 50 percent loss in 24 hours in oxygen deficient lake waters, (16). Most published reports indicate equivalent levels of degradation in terms of a few weeks to a few months rather

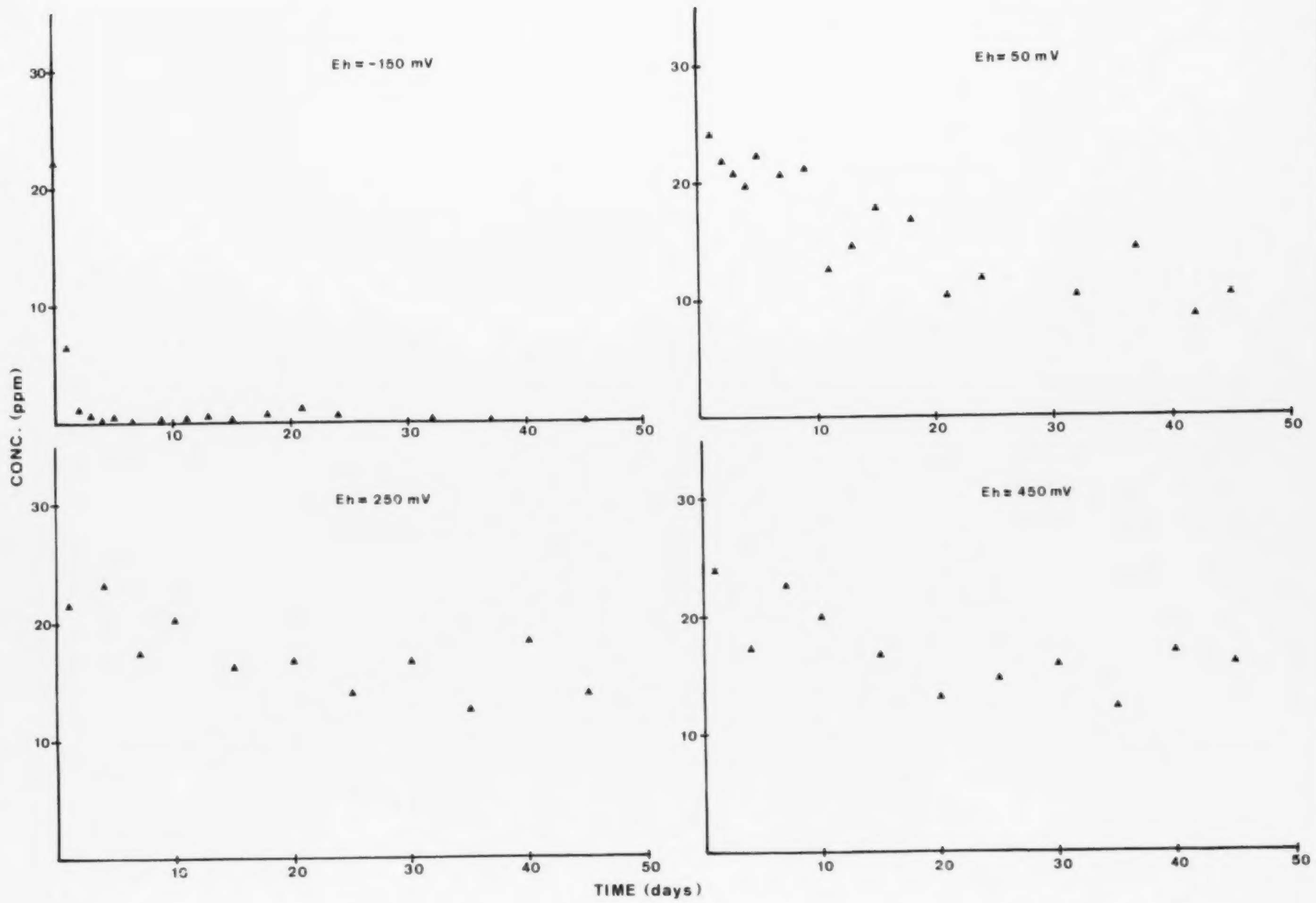

Figure 2. The Effect of Redox Potential (Eh) on the Recovery of Added DDT from Mobile Bay Sediment Suspension During a 45-Day Incubation at pH 6.0 (amended with 25 ppm DDT initially).

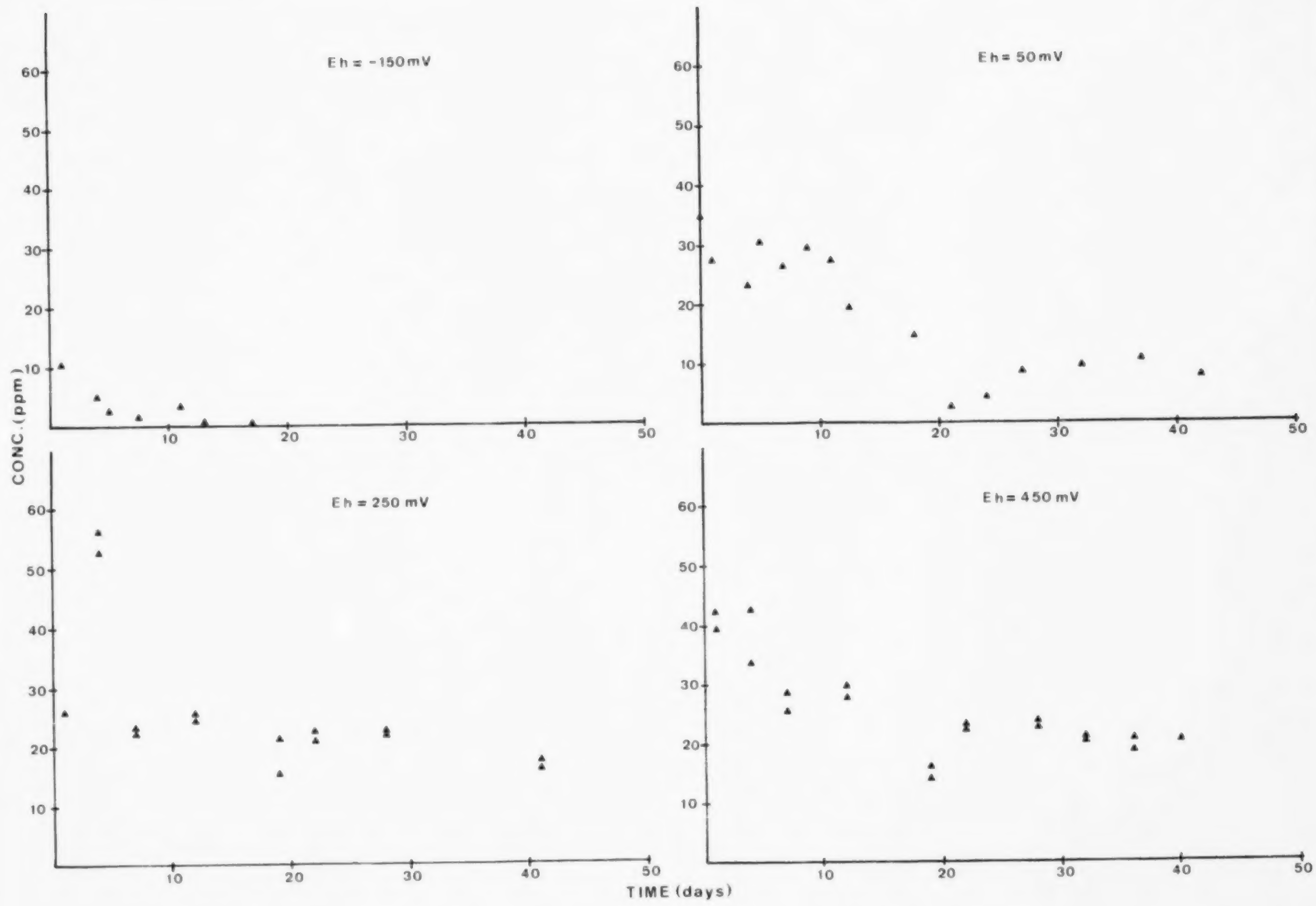

Figure 3. The Effect of Redox Potential (Eh) on the Recovery of Added DDT from Mobile Bay Sediment Suspension During a 45-Day Incubation at pH 7.0 (amended with 40 ppm DDT initially).

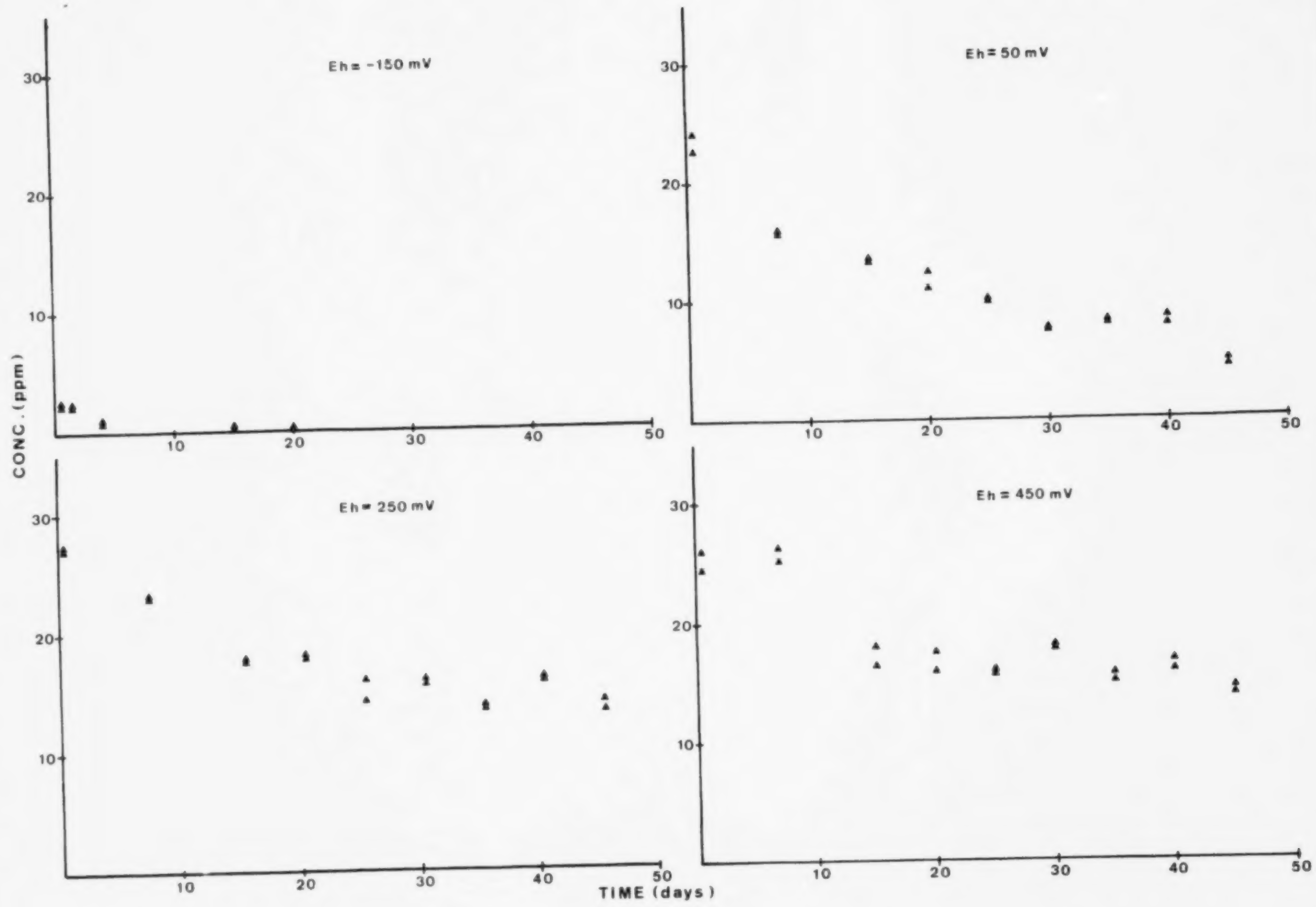

Figure 4. The Effect of Redox Potential (Eh) on the Recovery of Added DDT from Mobile Bay Sediment Suspension During a 45-Day Incubation at pH 8.0 (amended with 25 ppm DDT initially).

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than days. Thus we suspected experimental artifacts when first confronted with the apparent rapid degradation rates at -150 mv. There are several possible explanations to explain the initial low recovery of DDT under strongly reduced conditions: 1) drying artifacts, 2) the "bound residue effect", 3) volatilization in the continuous stream of nitrogen which purged the system, 4) adsorption on the glass walls of the flasks, tubing, electrodes, or the teflon coated magnetic stirring bar inserted in a short length of tygon tubing, and 5) unusually rapid degradation of DDT in the strongly reduced Mobile Bay sediment materials in this study. These points will be considered below.

To dry the sediment samples before Soxhlet extraction, we had previously determined that drying in the original glass storage bottles in a forced draft oven at 35 to 40°C for 2 or 3 days was satisfactory for both moderately reduced and well oxidized samples. Higher temperatures, which would effect more rapid drying, were not considered as this would have probably enhanced DDT volatilization as the sediment samples dried. The low recovery at -150 mv initially suggested to us that drying strongly reduced samples under air at elevated temperatures for 2 or 3 days may have contributed to enhanced degradation during drying. Because of this potential artifact, another technique was developed in which strongly reduced sediment samples could be dried in about 2 hours (see Development and Testing of Procedures, page 74). Incubations at -150 mv were repeated using the new drying technique, but this did not change the apparent degradation rates.

At this point, it is appropriate to mention the "bound residue effect" reported for parathion (1) and the possibility this phenomena is contributing to the apparent rapid degradation of DDT in this study. The bound residue effect refers to evidence that some proportion of the total amount of a compound, such as a pesticide, may be adsorbed so firmly to soil solids (mineral + organic) that it cannot be removed by the extraction procedures used to determine residues. Thus a lack of recovery or a decrease in recovery of a particular compound with time which is normally attributed to degradation may in part be due to "irreversible" adsorption. In carbon-14 studies, the proportion of added, labeled carbon recovered as CO_2 clearly indicates degradation. However, even in radiotracer studies, if all of the compound is not recovered as CO_2 and by solvent extraction, it is difficult to confirm whether the remaining label is associated with the parent molecule as a bound residue or as various degradation compounds. It is interesting to note that at 250 and 450 mv there was some decrease in DDT recovery during the first two weeks after which little further reduction occurred. Perhaps the "bound residue effect" contributed to this initial apparent loss in DDT. With parathion, this effect was reported to be twice as pronounced under flooded (anaerobic) conditions compared to nonflooded conditions (1). However, even

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where C-14 labelled compounds are used as mentioned above, it is not possible to establish whether the bound residue represents the parent compound or some degradation product. Thus the possibility that the parent DDT molecule became less susceptible to extraction procedures with time cannot be ignored, though the actual significance of "the bound residue effect" in this study cannot be determined. If, as for the reported parathion study, anaerobic conditions only doubled the "bound residue effect" over aerobic conditions, this process would not come close to explaining the large recovery differences observed between -150 mv and higher redox potentials.

The possibility of volatilization from the system was ruled out as no DDT was recovered when an organic solvent used in place of water in the air trap (page 22) was extracted for DDT.

The possibility that some adsorption occurred on the surfaces of the incubation vessel and its components cannot be ruled out as no effort was made to test for this. However, it seems unlikely that this would account for the observed treatment differences with DDT and, as will be evident from Figures 11, 12, and 13, adsorption to surfaces of the laboratory microcosms could not have occurred to a significant extent in the Kepone studies.

The fifth possibility is that the added DDT was indeed degraded within a few days at -150 mv. The chemical and microbial properties of the Mobile Bay sediment material at -150 mv are likely very different from most soil and sediment materials examined in DDT degradation studies, even those studies in which flooded or reduced conditions were imposed. In terms of texture (44 percent clay, 32 percent silt) and organic carbon content (1.8 percent), this material is not untypical of many soil and sediment materials. However, its sulfide content at -150 mv was above 400 ppm, potentially reactive iron (that quantity extracted by relatively mild chemical extractants) exceeded 37,000 μg/g and soluble iron levels at -150 mv were 3 and 330 μg/g oven dry solids (8:1 water:soil ratio) at pH 8.0 and 6.5 respectively (64). These properties and possibly others make the Mobile Bay sediment material different from most soils used for DDT studies.

Glass (33) concluded that the iron redox system in reduced soils is involved with DDT degradation and that redox systems other than iron may also contribute to DDT reduction by electron transfer processes. A relationship between ferrous iron levels and DDT degradation was established. In the work of Glass (33), the experimental combination of soils and treatments giving most rapid DDT degradation resulted in recovery of only 6 percent of initial DDT levels after 28 days. Although extraction procedures for iron differed somewhat from those used by Glass, we have previously shown that soluble and exchangeable (method similar

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to Glass's "soluble" iron) ferrous iron levels in Mobile Bay sediment material under a range of pH and oxidation-reduction conditions equaled or far exceeded iron levels in the reduced soil materials studied by Glass (33, 64). Thus the chemical properties of the Mobile Bay material may be more conducive to rapid DDT degradation than most materials studied and reported in the literature.

An obvious avenue to explore whether degradation accounted for the rapid loss in DDT is to examine the levels of known DDT degradation products at -150 mv, and especially levels of DDD as this compound is reported to be the predominant, first stage decomposition product under reducing conditions.

Although DDD levels extracted were not sufficient to account for the rapid disappearance of DDT during the first few days, DDD levels in the -150 mv treatment were 3 to 8 ppm during the first few days at all 3 pH levels compared to about 0.5 ppm for the two most oxidized treatments. Thus there is firm evidence that at least some DDT did degrade very rapidly under strongly reduced conditions, though a mass balance was not found. It is possible that some of the DDD rapidly formed was also subject to rapid degradation, or, that under strongly reducing conditions in Mobile Bay material, another intermediate was involved in DDT degradation.

DDD levels gradually decreased from elevated initial levels (due to DDT degradation) to 2 to 3 ppm after about 45 days in the -150 mv treatments (Figures 5-7). DDD levels at 50 mv were fairly constant during the incubations, though a slight tendency to increase was noted at most pH treatments. At 250 and 450 mv which represent poorly oxidized and well oxidized conditions, DDD levels were consistently around 0.5 ppm for the duration of the incubation.

DDE is reported to be the predominant degradation product of DDT under oxidized conditions. DDE levels ranged from essentially zero to around 1 ppm at all pH-redox potential combinations (Figures 8-10). Surprisingly, based on the literature, the -150 and 50 mv treatments (strongly and moderately reducing) exhibited higher DDE levels than the better oxidizing treatments. Though DDD production was greater than DDE production under the reduced treatments, it is apparent some DDE was produced under anoxic conditions during the rapid loss of DDT in the Mobile Bay sediment material. Because of the more rapid DDT degradation under reducing conditions, the DDE accumulated to slightly greater levels than in the better oxidized treatments where DDT was relatively stable.

In summary, DDT recovery from a spiked Mobile Bay sediment material decreased very rapidly under strongly reducing conditions such that greater than 90 percent could not be recovered

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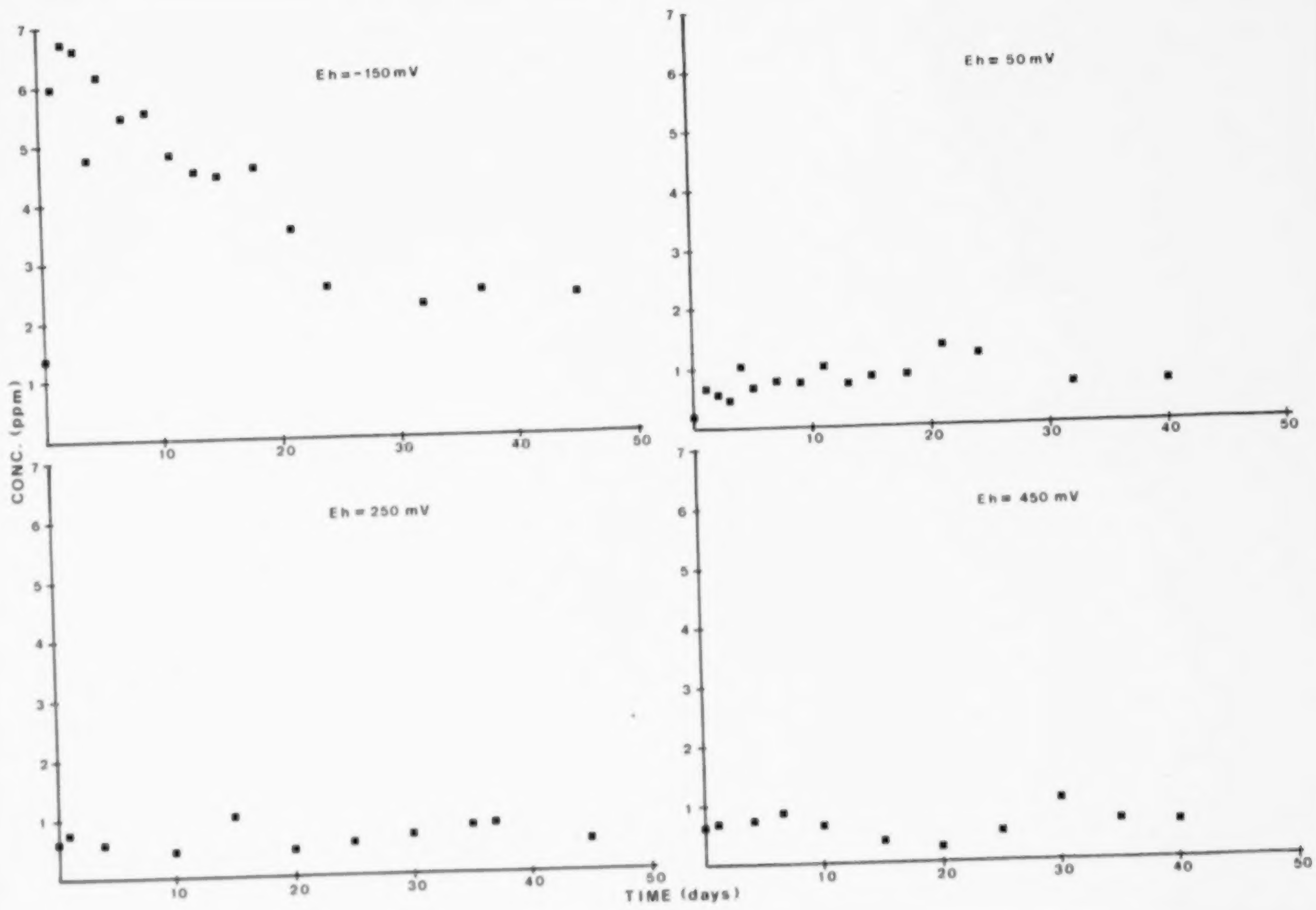

Figure 5. The Effect of Redox Potential (Eh) on the Recovery of DDD from Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 6.0.

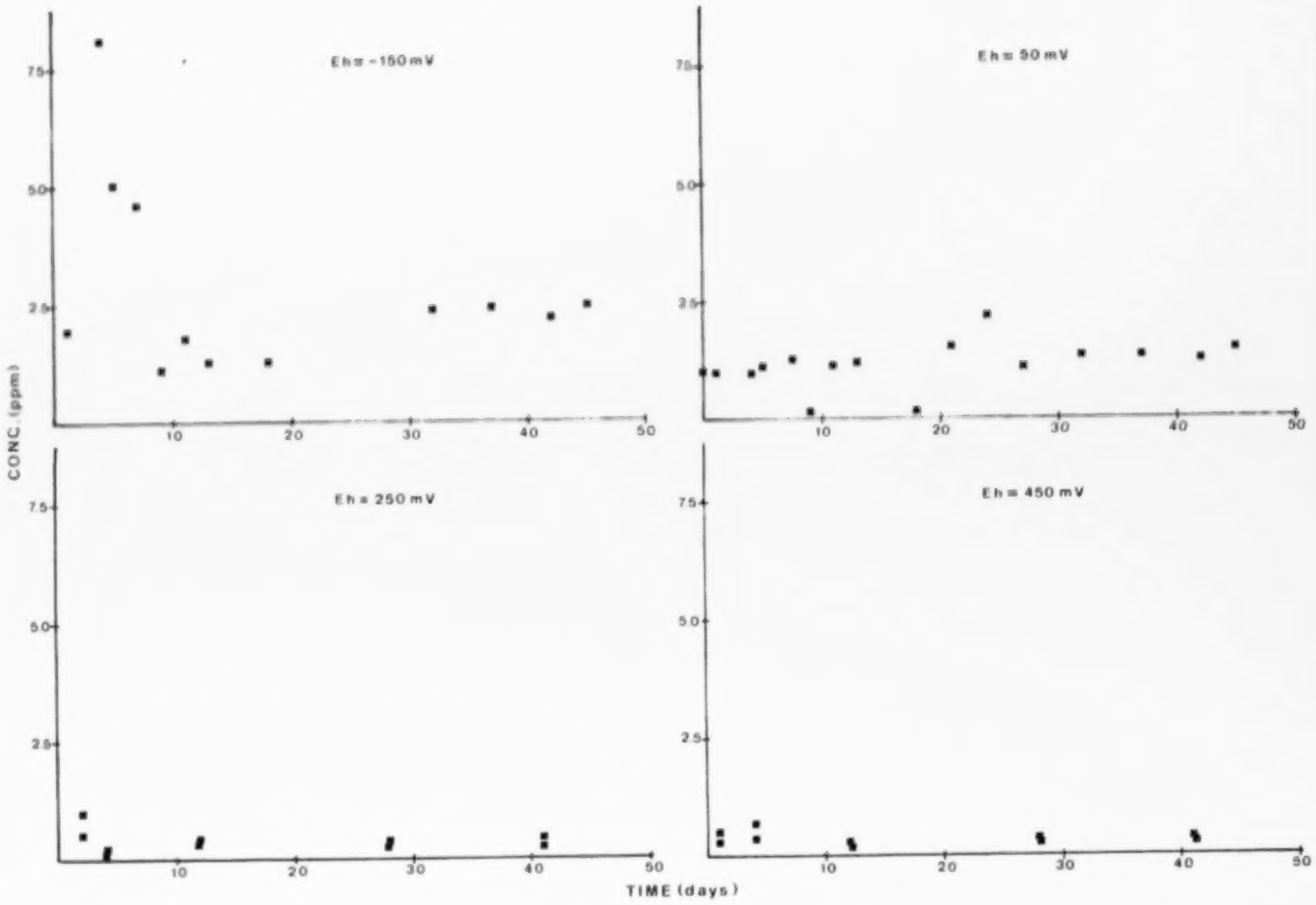

Figure 6. The Effect of Redox Potential (Eh) on the Recovery of DDD from a Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 7.0.

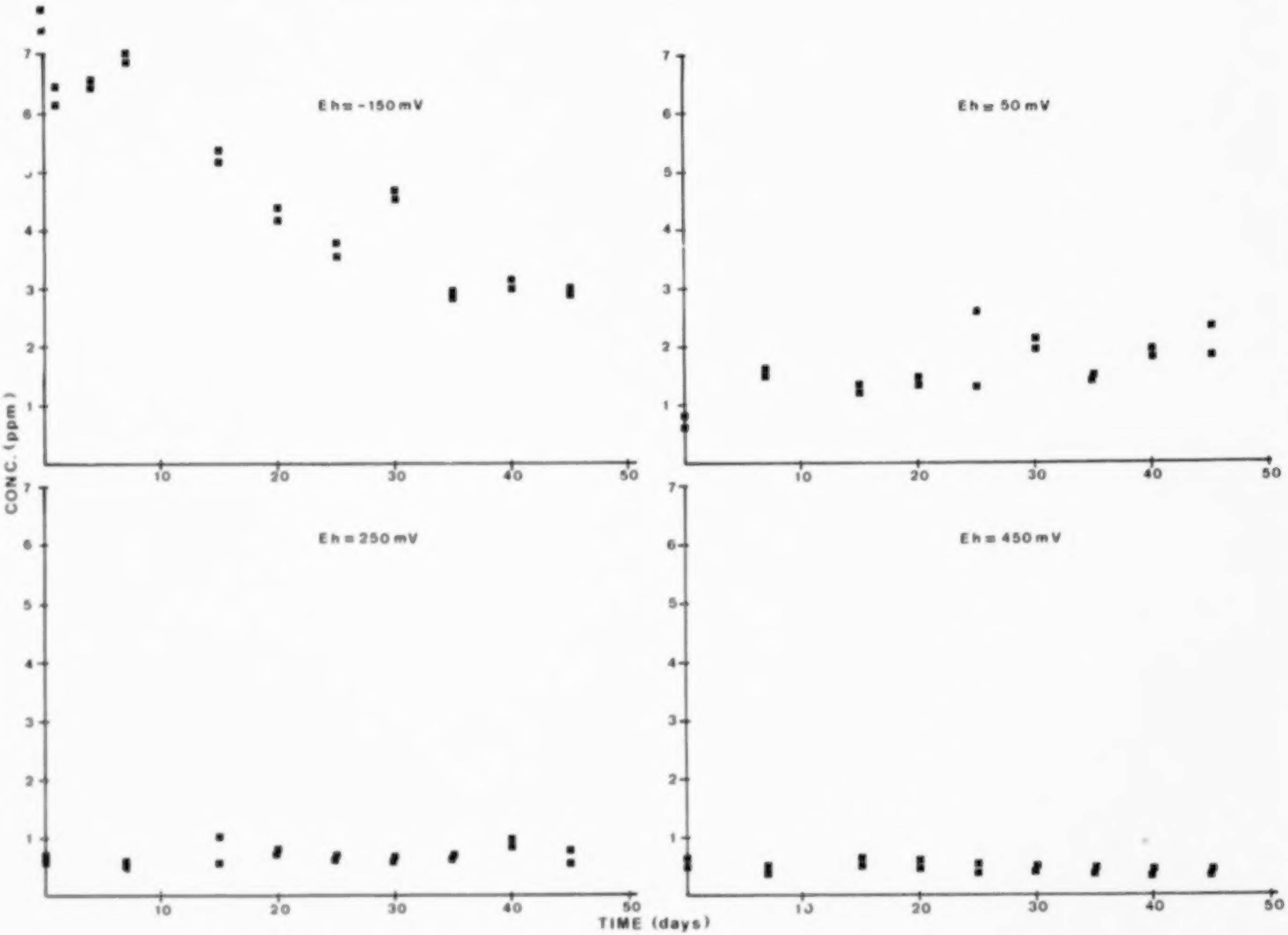

Figure 7. The Effect of Redox Potential (Eh) on the Recovery of DDD from a Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 8.0.

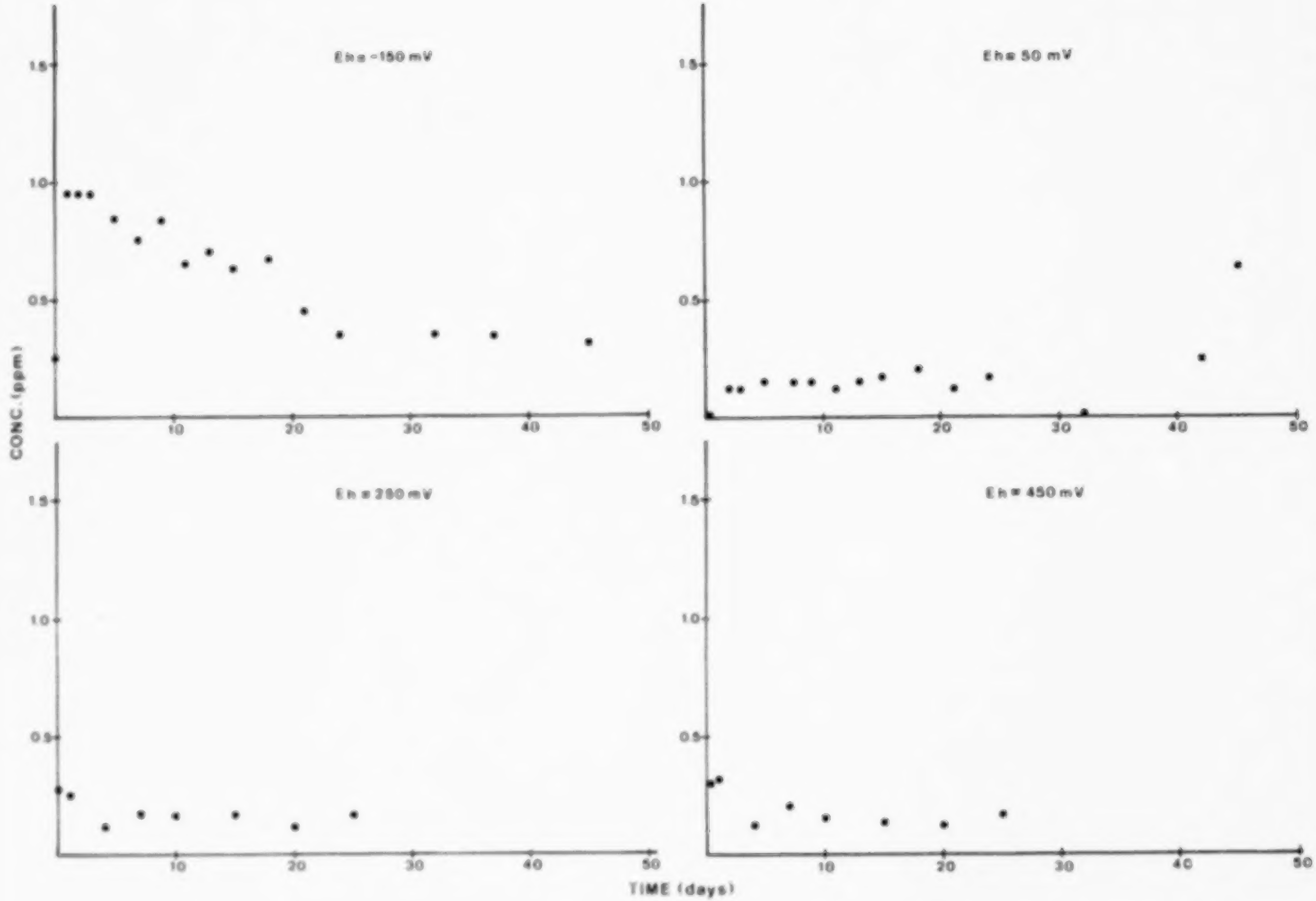

Figure 8. The Effect of Redox Potential (Eh) on the Recovery of DDE from a Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 6.0.

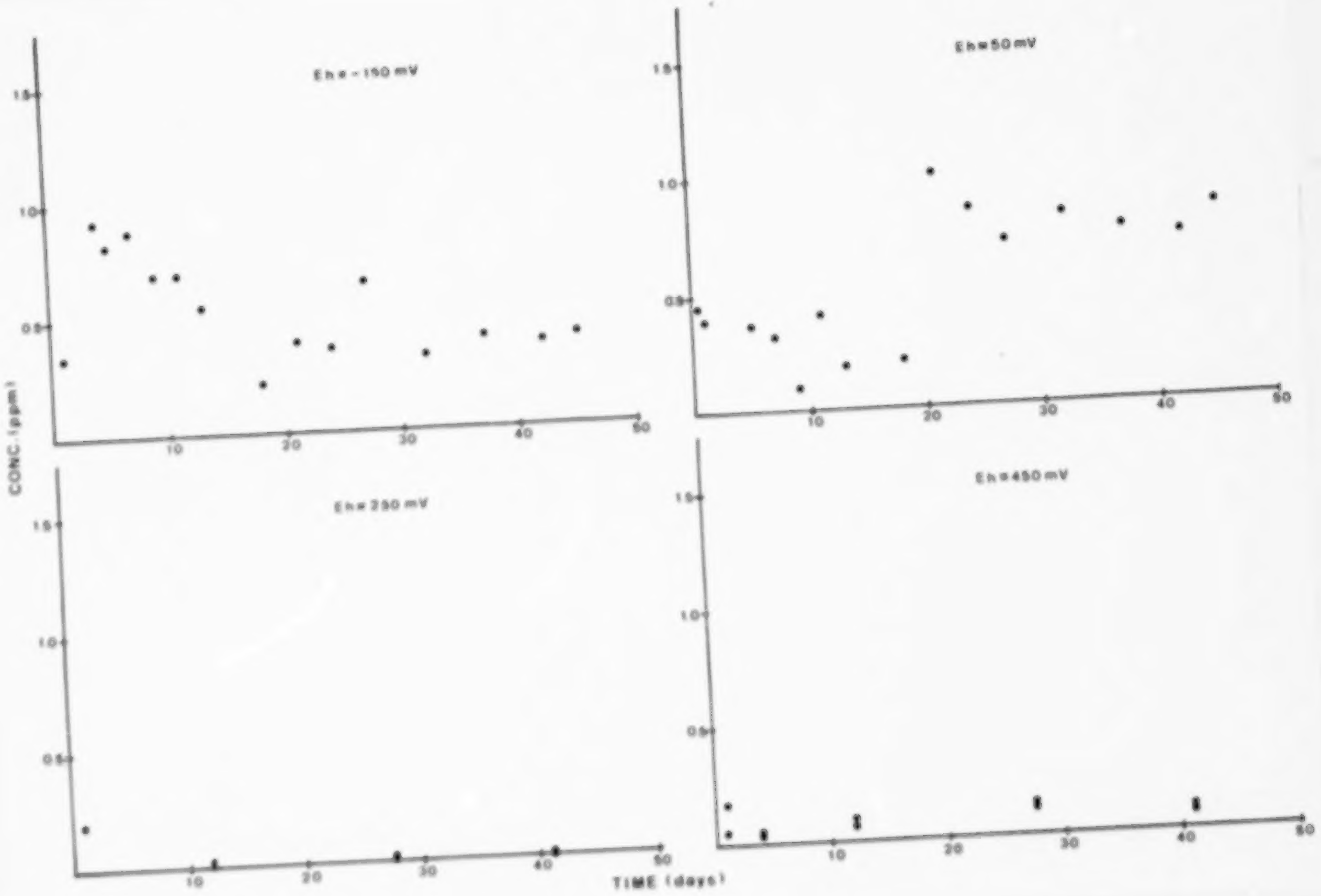

Figure 9. The Effect of Redox Potential (Eh) on the Recovery of DDE from a Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 7.0.

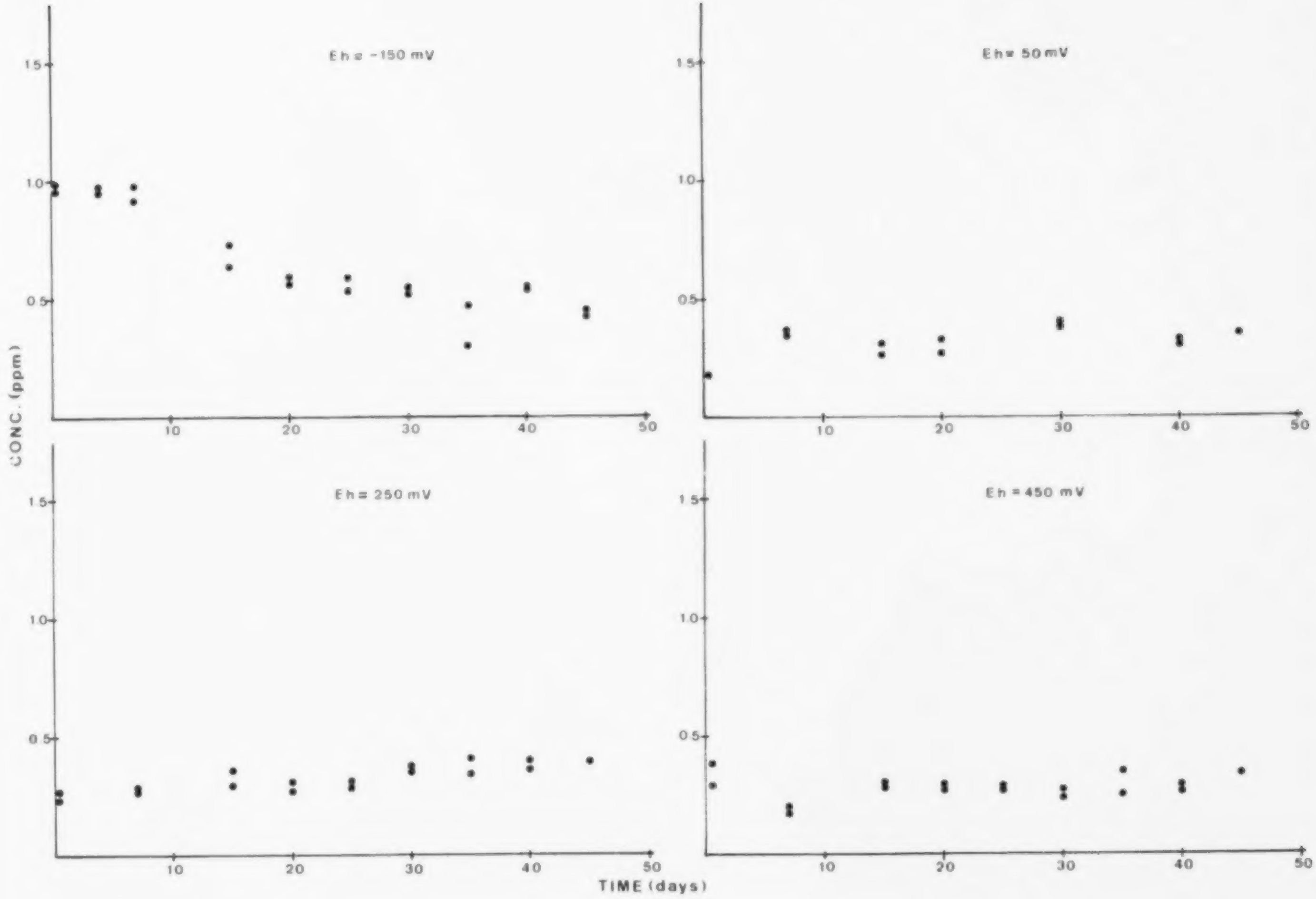

Figure 10. The Effect of Redox Potential (Eh) on the Recovery of DDE from a Mobile Bay Sediment Suspension Amended with DDT During a 45-Day Incubation at pH 8.0.

after as little as 5 days. The evidence indicates this loss is due to a considerable extent to rapid DDT degradation. A less rapid loss (two-thirds in about 45 days) was noted at 50 mv (moderately reduced conditions) while DDT appeared fairly stable under better oxidized conditions after an unexplained decrease of about one third of initial levels during the first two weeks. Where DDT loss was rapid under reduced conditions, both DDD and DDE levels increased with DDD production predominating.

Only at 50 mv was there an indication that a degradation product was accumulating. However, the very slight increase in DDD levels noted with time was not equal to the rate of DDT loss from these treatments. Thus it is believed DDD levels would begin to decline within another month or so when it appeared DDT loss would essentially be complete at moderately reduced conditions.

KEPONE

Figure 11 indicates the effect of redox potential on the levels of Kepone in James River sediment suspensions incubated at pH 5.0 for 51 days. At redox potentials of -150, +50, and +250 mv (strongly reduced to weakly oxidized), initial Kepone recovery was 17 to 18 μg/g while initial recovery was 15 to 16 μg/g at 250 mv (well oxidized). During the 51 day incubation, there appeared to be a very gradual decline in Kepone levels to about 12 to 13 μg/g in all treatments except for the Day 51 -150 mv data which increased, possibly due to experimental variability.

Figure 12 indicates Kepone levels in James River sediment suspensions incubated at pH 7.0 for 52 days. During the initial few days, 16 to 22 μg/g Kepone was recovered from all redox potential treatments (most of these data were clustered around 20 μg/g). There is some scatter in the data, but these data suggest little if any Kepone degradation at any redox potential level during the 52 day incubation. As observed for pH 5.0, there is no evidence that oxidation-reduction levels have any effect on Kepone degradation.

Figure 13 gives the effect of redox potential on Kepone levels in James River sediment suspensions incubated at pH 8.0. For unknown reasons, considerable variability was noted between sampling dates and between subsamples, especially at 450 and 250 mv. After 70 days, Kepone recovery had decreased from near 20 μg/g to 10 μg/g at all redox potential levels. Since there is a substantial decrease in Kepone levels for only the last sampling date at pH 8.0 (which was about two weeks beyond any other sampling date at any pH), we are not sure if this represents some experimental variability or the beginning of degradation after a lag phase of about 2 months. A gradual decline was

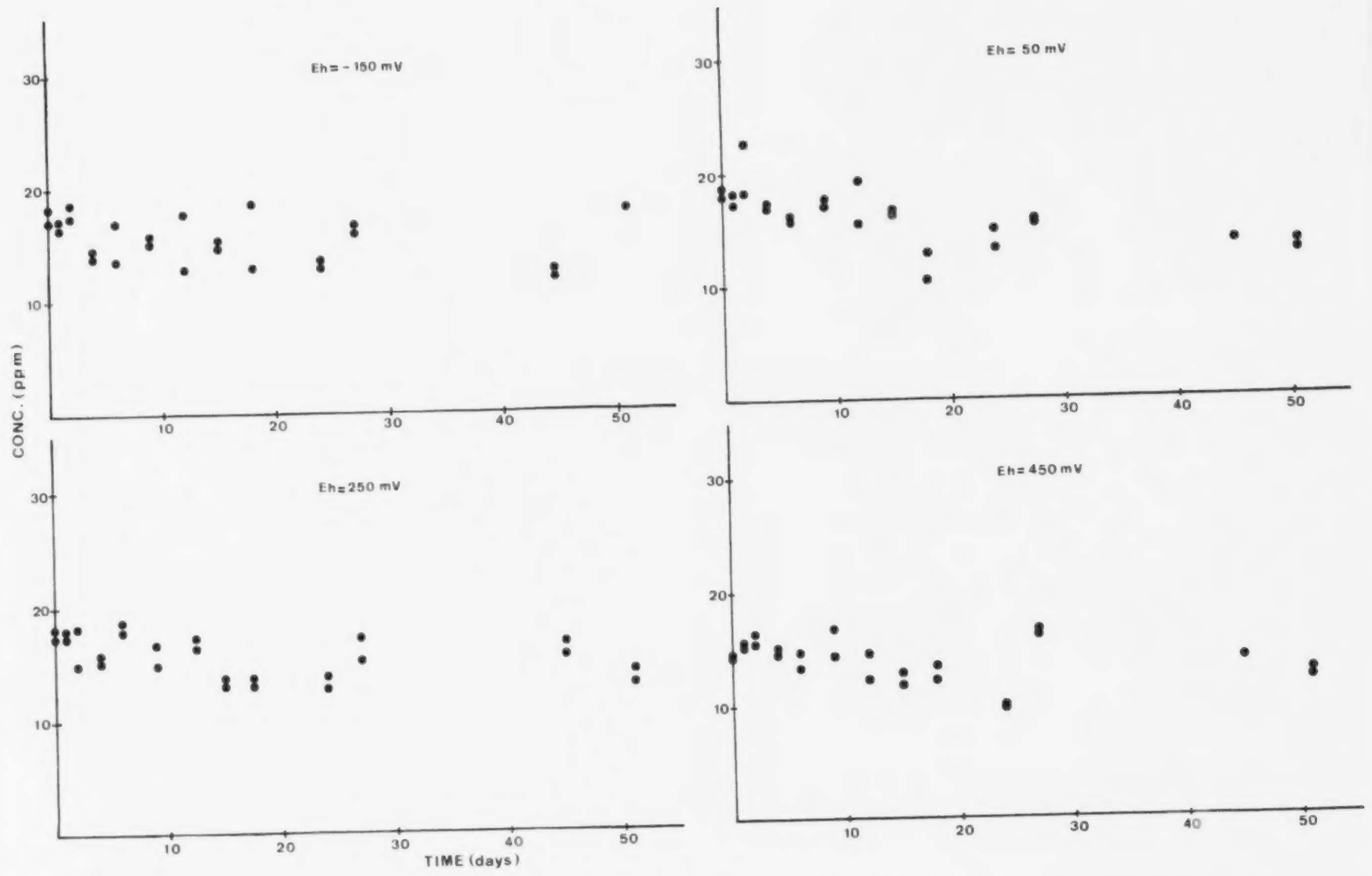

Figure 11. The Effect of Redox Potential (Eh) on the Recovery of Added Kepone from James River Sediment Suspension During a 51-Day Incubation at pH 5.0 (amended with 21 ppm Kepone initially).

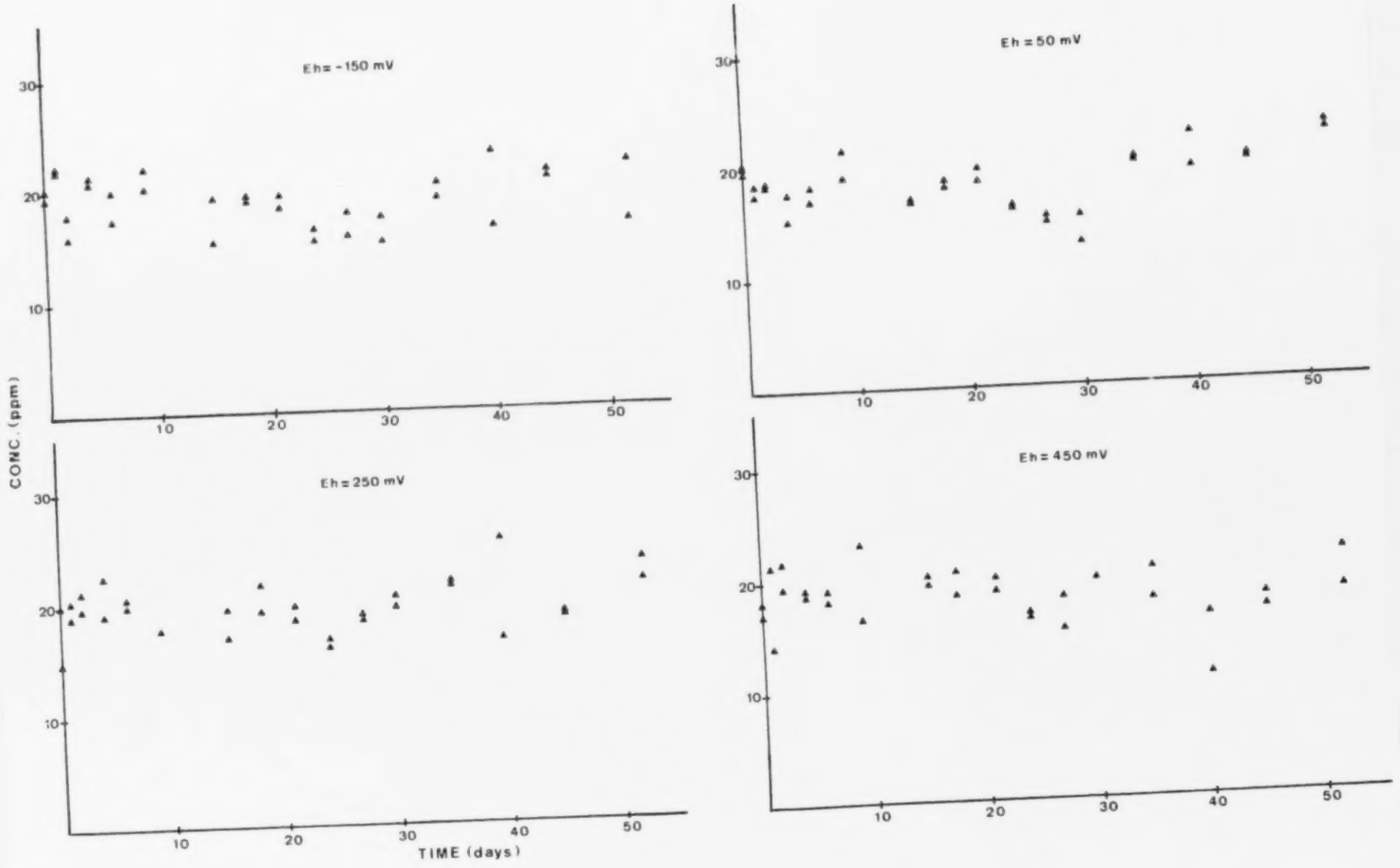

Figure 12. The Effect of Redox Potential (Eh) on the Recovery of Added Kepone from James River Sediment Suspension During a 52-Day Incubation at pH 7.0 (amended with 21 ppm Kepone initially).

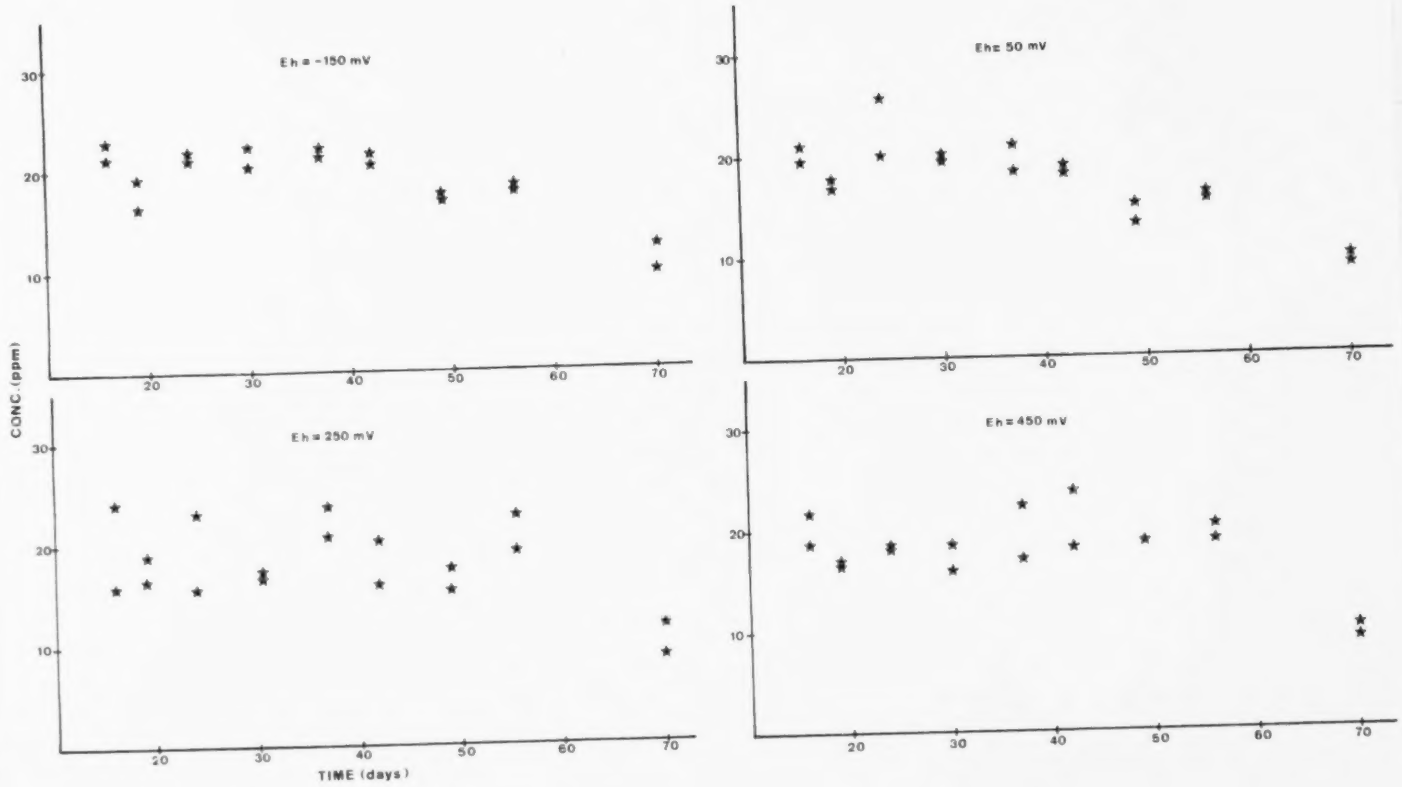

Figure 13. The Effect of Redox Potential (Eh) on the Recovery of Added Kepone from James River Sediment Suspension During a 70-Day Incubation at pH 8.0 (amended with 21 ppm Kepone initially).

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noted for the two most reducing (-150 mv and 50 mv) sediment materials whereas the decline, if real, was more abrupt in the better oxidized suspensions. As found at pH 5.0 and pH 7.0, there is no clear indication that oxidation-reduction conditions affected Kepone degradation at pH 8.0. However, the data suggests that Kepone degradation may be enhanced somewhat at pH 8.0 relative to pH 7.0 and 5.0 and that this loss may occur only after a considerable lag period.

PERMETHRIN

A preliminary study conducted on the effects of controlled pH and oxidation conditions indicated substantial effects of both parameters on the persistence of Permethrin in the Olivier silty clay loam. After obtaining oxidized and reduced conditions by continuous air or nitrogen purging for several days, the pH of the suspensions was adjusted to 5.5 and 7.5 and several additional days of equilibration permitted before the samples were spiked with 17.8 μg/g Permethrin. Immediately after spiking, approximately 14 to 15 μg/g Permethrin was recovered from all treatments (Table 3). At 5 days, Permethrin disappearance appeared to be a function of both pH and oxidation levels. These trends continued until the experiment was terminated at 20 days. At 20 days, Permethrin had essentially disappeared under oxidized conditions at pH 5.5 while under reducing conditions levels only decreased to around 12 μg/g. Both oxidation levels at pH 7.5 resulted in intermediate degradation rates. Approximately 6.0 ppm were recovered under reducing conditions and 3.0 ppm were recovered under oxidizing conditions at 20 days.

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TABLE 3. RECOVERY OF PERMETHRIN FROM AN OLIVIER SOIL SUSPENSION INCUBATED UNDER CONTINUOUS NITROGEN OR AIR PURGING AT pH 5.5 and pH 7.5

	pH 5.5		pH 7.5	
Day	Nitrogen	Air	Nitrogen	Air
	Permethrin, μg/g			
5	12.5	2.0	7.7	6.9
17	12.5	0.1	6.1	3.3
20	12.5	0.3	6.1	3.1

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Unlike Kepone persistence which showed little response to either pH or oxidation-reduction conditions, or DDT which responded primarily to oxidation levels, this preliminary study indicated Permethrin persistence was substantially affected by both pH and oxidation-reduction conditions.

Another study with Permethrin was conducted using four controlled redox potential levels (-150, +50, +250, and +450 mv) and 3 pH levels (5.5, 7.0, and 8.0). These data are presented in Figures 14-16.

Again it is apparent that both pH and redox potential influenced the loss of Permethrin from these systems. Under well oxidized conditions (+450 mv) Permethrin had essentially disappeared (less than 0.5 ppm) at all pH levels after 19 days. Under strongly reducing conditions, approximately one third was lost from the pH 5.5 treatment while about two thirds of initial levels were lost at pH 8.0 after 26 days. In this study there was a tendency for Permethrin to degrade more quickly with increasing pH under both oxidizing and reducing conditions.

The data in Figures 14-16 include the total Permethrin content of the samples (the sum of the cis and trans isomers). Because a gas chromatography column was selected which would separate the cis and trans isomers, it was possible to look at the effects of pH and redox potential on the degradation of the individual isomers. Table 4 indicates the percentage of total Permethrin in the trans isomer for two sampling dates under strongly reducing (-150 mv) and well oxidized (+450 mv) conditions. This information could be calculated for every sample in this study, but the information in Table 4 summarizes the important physicochemical effects noted. Day 1 (Day 2 for pH 8) was selected to give the ratio near the beginning of the incubation. Day 15 (Day 14 for pH 7.0) was selected for inclusion in this table because this was the last sampling date before Permethrin levels decreased to very low levels in the oxidized treatments.

From Table 4 it is apparent that both pH and oxidation have substantial effects on the relative degradation of the cis and trans isomers. Increasing pH (from 7 to 8) and increasing oxidation conditions favored the loss of the trans isomer relative to the cis. There was relatively little change in the ratio under reduced conditions at pH 5.5 and 7.0 during the first 15 days.

The results of this study confirm what is already known about Permethrin in that long-term accumulation of residues will not pose an environmental threat. However, this study does indicate that physicochemical conditions of the environmental compartment receiving residues can have a substantial effect on the persistence of Permethrin during the course of a few weeks

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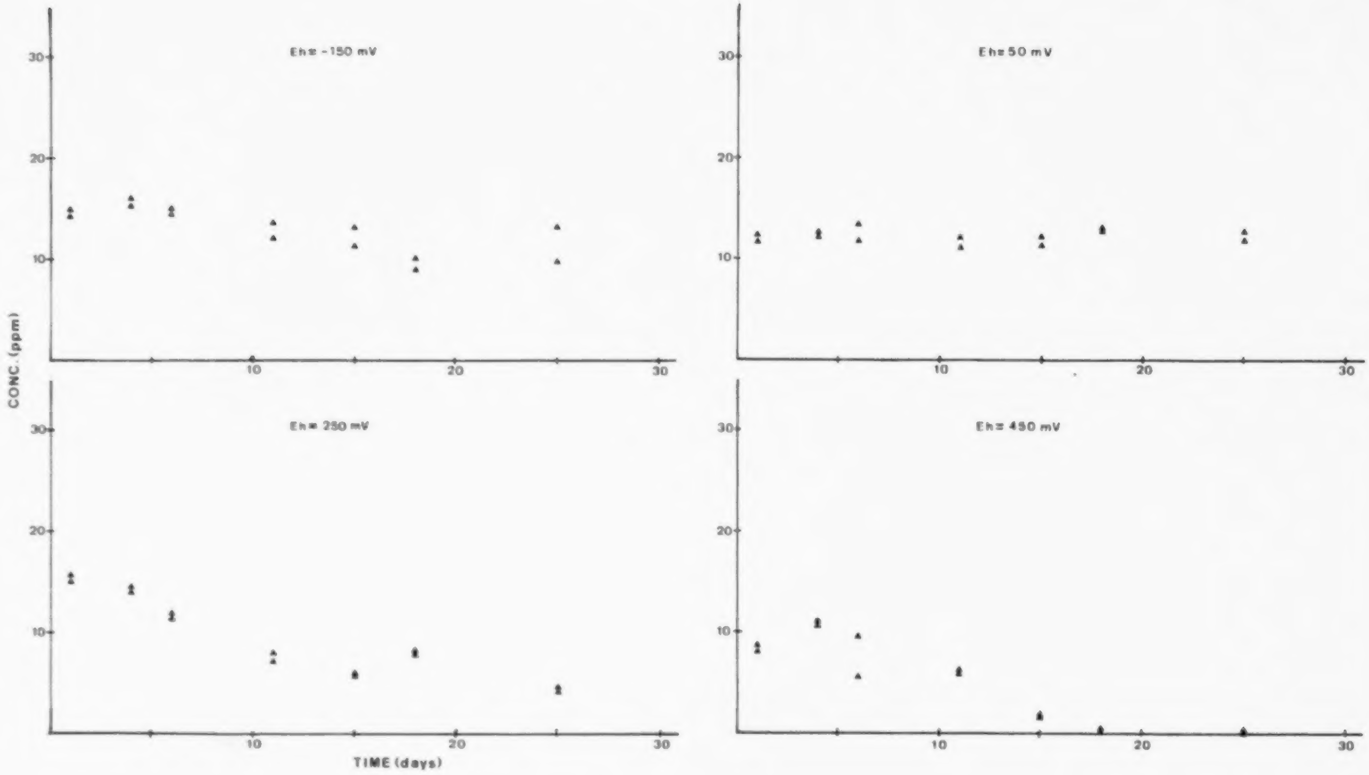

Figure 14. The Effect of Redox Potential (Eh) on the Recovery of Added Permethrin from an Olivier Soil Suspension During a 25-Day Incubation at pH 5.5 (amended with 15-17 ppm Permethrin initially).

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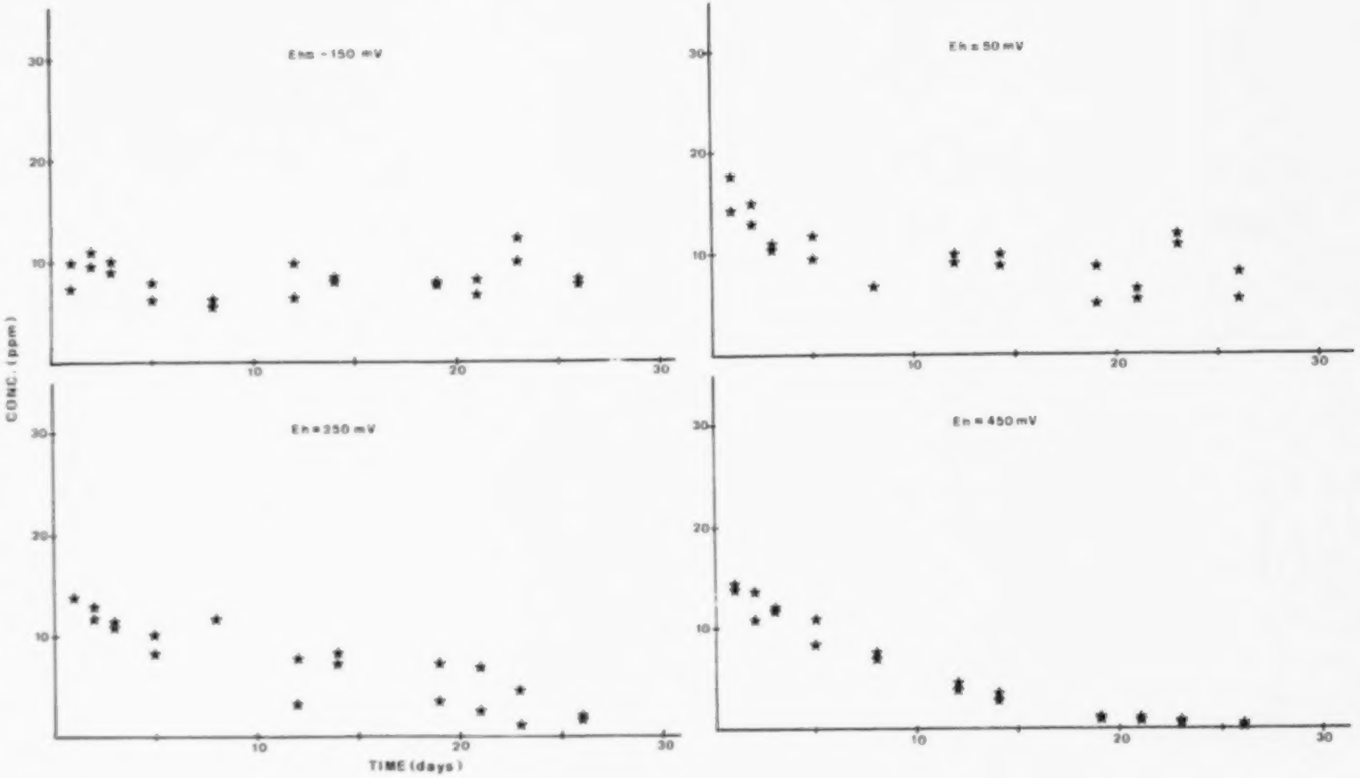

Figure 15. The Effect of Redox Potential (Eh) on the Recovery of Added Permethrin from an Olivier Soil Suspension During a 26-Day Incubation at pH 7.0 (amended with 15-17 ppm Permethrin initially).

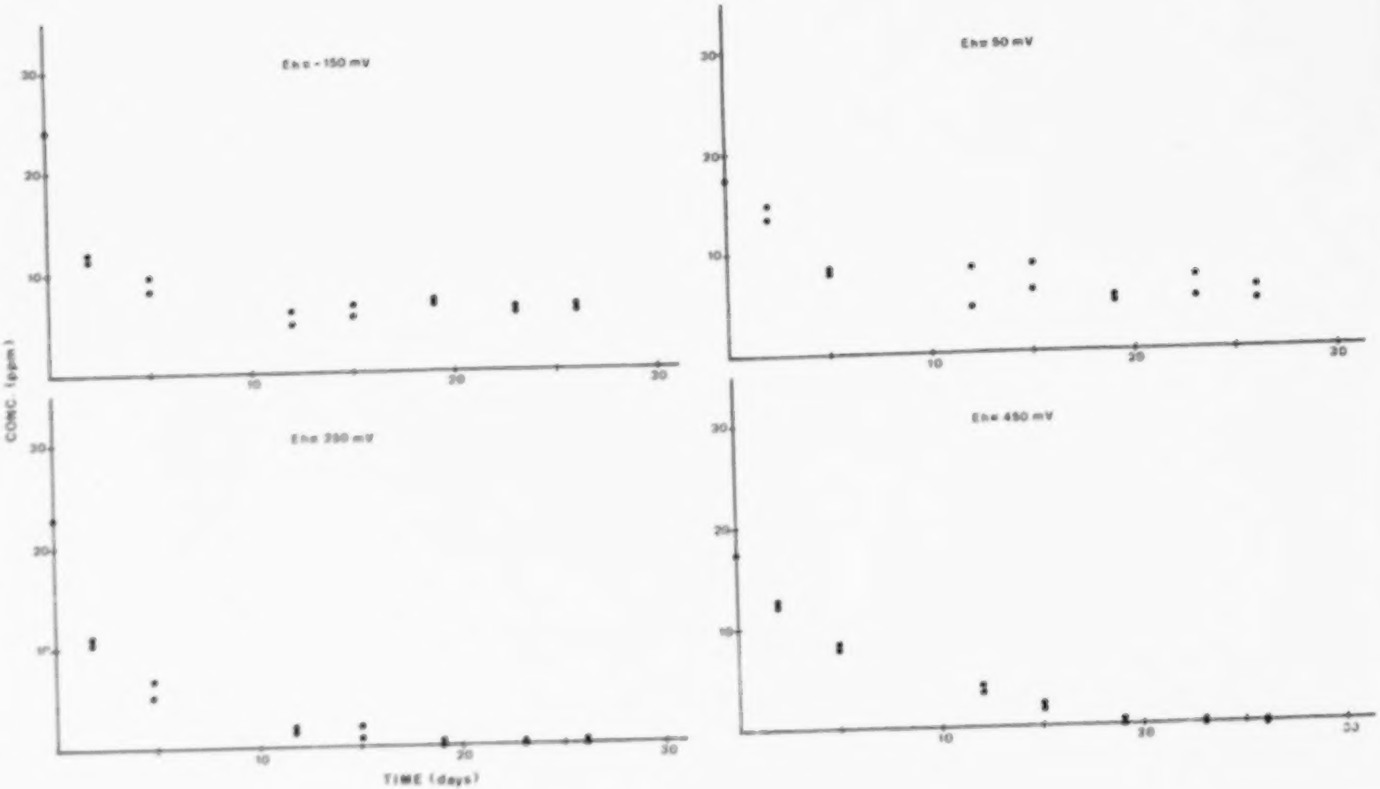

Figure 16. The Effect of Redox Potential (Eh) on the Recovery of Added Permethrin from an Olivier Soil Suspension During a 26-Day Incubation at pH 8.0 (amended with 15-17 ppm Permethrin initially).

TABLE 4. EFFECT OF pH AND OXIDATION LEVELS ON THE RELATIVE DEGRADATION OF THE CIS AND TRANS ISOMERS OF PERMETHRIN FOR SELECTED SAMPLING DATES AND REDOX POTENTIAL TREATMENTS

	Day 1 of Incubation (Day 2 for pH 8)		Day 15 of Incubation (Day 14 for pH 7.0)	
pH	-150 mv	+450 mv	-150 mv	+450 mv
	peak height trans/peak height cis + trans, %			
5.5	64.2[†] ± 0.0[‡]	62.6 ± 1.5	64.3 ± 0.7	24.4 ± 0.8
7.0	65.7 ± 0.3	62.4 ± 0.1	64.0 ± 0.3	20.0 ± 0.0
8.0	61.6 ± 0.1	56.6 ± 0.1	50.0 ± 0.0	14.8 ± 3.2

[†] Mean of two subsamples (extraction of two separate soil samples from the same experimental incubation vessel).

[‡] Standard deviation.

to a few months. Strongly reducing conditions characteristic of sediments will enhance the persistence of Permethrin. This is similar to results for Cypermethrin, another synthetic pyrethroid, which has been found to degrade more quickly under aerobic conditions than waterlogged conditions in a sandy loam soil (60).

Our results also correspond with one study of Permethrin in which approximately 60 percent of the ^{14}C activity of labelled Permethrin in an oxidized Hagerstown silty clay loam was trapped as $^{14}CO_2$ vs. 1 percent from the anaerobically incubated soil. In the system used by Kaufman et al., (65) it was not determined if more of the ^{14}C activity from degradation products might have been present in the aqueous phase. In our studies, both the water and soil were extracted for the parent compound and it is demonstrated conclusively that Permethrin is degraded more rapidly under oxidized conditions.

Considering the documented high toxicity of certain synthetic pyrethroids to a number of aquatic and benthic organisms (63), it should be kept in mind that the strongly reduced environs of many sensitive benthic species favors some increase in the persistence of residues which may adversely affect these populations should residues be transported from adjacent fields in surface runoff. On the other hand, residues in upland soils will degrade more quickly. Thus the length of time between Permethrin application and a significant runoff event will strongly influence the potential for adverse environmental effects of Permethrin residues in wetlands or sediment-water systems.

The FMC Corporation (66) found the cis isomer present in higher concentrations in treated cotton plot soil than the trans isomer. It was suggested either the cis isomer was more persistent or that this isomer was more easily removed from treated cotton leaf surfaces and transported to the soil. Surface runoff samples also contained a higher proportion of the applied cis than trans isomer and again it was suggested either greater persistence or mobility of the cis isomer accounted for these differences. Our work suggests that soil oxidation conditions probably contributed to enhanced degradation of the trans isomer as cotton is usually grown in well oxidized soils.

SECTION 7

AUXILIARY STUDIES

DDT DEGRADATION UNDER AEROBIC, ANAEROBIC, AND ALTERNATE AEROBIC/ CONDITIONS

Materials and Methods

Mobile Bay sediment material was preincubated as suspensions under continuous air purging or nitrogen purging for a 2-week period to obtain oxidizing and reduced suspensions. After two weeks, four equal 1800 gram aliquots (200 grams oven dry solids plus 1600 grams water) of the reduced material were spiked with DDT at a level of 26.6 μ g/g (oven dry solids basis). Two of these suspensions were incubated under continuous nitrogen purging and two were incubated under alternate nitrogen/air purging (two week cycles) for 3 months. At the same time, two spiked, continuously aerobic suspensions were set up. Thus each of the three treatments was replicated. After 3 months, the aqueous phase was separated by centrifugation and filtration and analyzed for the DDT, DDD, and DDE according to published methods (67). DDT and its metabolites were extracted from the sediment phase and analyzed using methods described elsewhere in this report.

Results and Discussion

Loss of DDT from the solid sediment phase was greatest and almost complete under continuous reduced conditions (Table 5). Continuous oxidizing conditions resulted in the highest levels of residual DDT (approximately 4.3 μg/g). The alternating aerobic-anaerobic treatment gave intermediate levels (approximately 1.1 μg/g). As expected, DDD levels were greatest in the anaerobic treatment. DDD was not detected in the aerobic suspensions and was present in intermediate amounts in the suspension solids subject to alternate aerobic/anaerobic conditions. DDE levels were very similar in all three treatments, with the aerobic treatment containing the largest quantity by a small margin and the continuous anaerobic treatment the smallest quantity of DDE after 3 months. Given 88-92 percent recovery from samples extracted immediately after spiking, this study suggests either a significant "bound residue effect" or that most of the DDT (as well as DDD and DDE assuming these are the

TABLE 5. DDT, DDD, AND DDE RECOVERY FROM A DDT-AMENDED MOBILE BAY SEDIMENT SUSPENSION INCUBATED UNDER CONTINUOUS AEROBIC, ANAEROBIC, AND ALTERNATE AEROBIC-ANAEROBIC CONDITIONS FOR 3 MONTHS

Sediment Levels[†], µg/g oven dry solids

Oxidation-Reduction Conditions	Compound		
	DDT	DDD	DDE
Aerobic	4.32[¶] ± 0.05[‡]	0	0.10 ± 0.01
Anaerobic	0.09 ± 0.02	0.58 ± 0.03	0.08 ± 0.00
Alternate Aerobic-Anaerobic	1.13 ± 0.13	0.38 ± 0.13	0.10 ± 0.01

Dissolved Levels, µg/ℓ

Oxidation-Reduction Conditions	DDT	DDD	DDE
Aerobic	0.58 ± 0.32	nd[ε]	0.05 ± 0.02
Anaerobic	0.08 ± 0.11	nd	0.19 ± 0.01
Alternate Aerobic-Anaerobic	0.33 ± 0.23	nd	0.14 ± 0.15

[†] Initially spiked with 26.6 µg/g DDT

[¶] Mean of replicated treatments

[‡] Standard deviation

[ε] Not detected

primary initial degradation products of DDT) were degraded to other unknown compounds during the 3 month incubation. Thus as DDT is removed from these Mobile Bay suspensions, there is not an equivalent accumulation of the two primary degradative compounds.

The dissolved DDT in the aqueous phase after 3 months is also indicated in Table 5. No dissolved DDD could be detected. Dissolved DDT and DDE levels in the three treatments were very low and exhibited greater experimental error compared to quantities extracted from the sediment phase. The relative quantities of dissolved DDT and DDE were, as expected, similar to sediment extractable levels.

The results of this preliminary study are in general agreement with literature findings in that anaerobic conditions are conducive to most rapid loss of DDT while favoring DDD formation over DDE. Aerobic conditions resulted in the slowest loss of DDT and favored DDE formation over DDD. In this particular study, there were less differences in levels of the three compounds due to imposed oxidation-reduction conditions at the end of 90 days than expected from the literature. Alternate anaerobic/aerobic conditions resulted in concentrations between those found for continuous aerobic or anaerobic treatments. This small study was initiated with the hypothesis that frequent changes in redox potential may be accompanied by rapid DDT degradation due to associated transformations between ferrous iron and ferric oxyhydroxides. Iron in soils and sediments has been implicated in mediating electron transfer processes involved with DDT degradation (33). Although the abundance of potentially reactive iron in the Mobile Bay sediment material relative to most soils used for DDT degradation studies may have enhanced degradation, frequent chemical transformations of the iron between oxidized and reduced forms were not associated with enhanced degradation over physicochemical conditions in which the iron was not undergoing redox transformations.

ADSORPTION OF ^{14}C-LABELLED DDT BY DIFFERENT COMPONENTS OF SEDIMENT PARTICULATES

Materials and Methods

Two sediments were used in this study. A sediment material was collected from the Calcasieu River ship channel near the I-210 bridge in Lake Charles, Louisiana. The Mobile Bay sediment material was the same used for DDT sediment degradation studies. The effects of selective removal of different components on adsorption of ^{14}C-labelled DDT were studied for both sediments.

The sediments were first washed several times to remove soluble salts and soluble low molecular weight organic molecules. A portion of this material was equilibrated with labelled DDT and the remainder treated with 30% hydrogen peroxide on a hot plate to remove the insoluble organic matter which is an important adsorptive component of sediments and soils. After the organic matter was destroyed, residual sediment-solids were washed several times with deionized water to remove excess hydrogen peroxide, soluble salts and free acid left from the hydrogen peroxide and a portion used for the labelled DDT adsorption studies.

The remainder of the sediment material treated to remove soluble salts and organic matter was subjected to sodium dithionate-sodium citrate-sodium bicarbonate treatments as described by Jackson (68) to remove iron oxyhydroxides. Original untreated sediment material was used to compare the adsorption of ^{14}C-labelled DDT of the whole sediment with the treated sediment materials.

Duplicate 10 gram portions of air dry, pretreated sediments were placed in 40 ml centrifuge tubes containing 20 ml of ^{14}C-labelled (0.05 μCi/ml) DDT solution (0.1 ppm and 1.00 ppm). The contents of the centrifuge tubes were shaken on a horizontal box shaker for 2 hours, centrifuged, and the clear supernatant solution was removed and stored for ^{14}C counting by liquid scintillation.

The residual sediment in the centrifuge tubes was extracted with 20 ml of hexane-acetone (3:1) for two hours, centrifuged, and the supernatant solution was removed for liquid scintillation counting. The results are expressed as percent of added ^{14}C measured in solution and extracted by the hexane-acetone extractant. It was assumed that measured ^{14}C represented the added parent compound.

Results and Discussion

Table 6 shows the percent of added ^{14}C-labelled DDT recovered in solution and extracted by the hexane-acetone mixture in Calcasieu River and Mobile Bay sediments. Almost all of the added ^{14}C-labelled DDT was adsorbed on sediment solids in both the sediment materials. DDT levels in solution was little affected by soluble salts removal. Recovery in solution did increase somewhat (from about 0.6 percent to just over 1 percent) where organic matter was removed, but further treatment to remove ferric oxyhydroxides had no apparent influence on soluble, labelled DDT in these sediment materials.

The hexane-acetone extractable ^{14}C-labelled DDT was significantly affected by the treatments to remove sediment components in both sediment materials. The hexane-acetone extractable ^{14}C-DDT increased from 27 to around 45 percent and 21 to around 70 percent, respectively at 0.1 ppm and 1.0 ppm addition levels after the organic matter was removed in the Calcasieu River sediment. This indicates organic matter is playing an important role on the adsorption of DDT in this material. It appears that soluble salts and iron oxyhydroxides are not affecting the adsorption as their removal did not significantly change the hexane-acetone extractable ^{14}C-labelled DDT in the Calcasieu River sediment material. The Mobile Bay sediment material appeared to respond differently depending on initial DDT concentration. The hexane-acetone extractable DDT increased with the removal of both soluble salts and organic matter from about 41 percent to 61 and 76 percent, respectively. At 1.0 ppm initial DDT concentration, there was an apparent decrease in solvent extractable DDT as adsorptive components were removed. The hexane-acetone extractable DDT was different

TYPING GUIDE SHEET

TABLE 6. THE EFFECT OF INITIAL DDT CONCENTRATION AND SELECTIVE REMOVAL OF SOLUBLE SALTS, ORGANIC MATTER, AND IRON OXIDES ON WATER SOLUBLE AND ORGANIC SOLVENT EXTRACTABLE DDT IN CALCASIEU RIVER AND MOBILE BAY SEDIMENT MATERIALS

	Calcasieu River Sediment Material								Mobile Bay Sediment Material							
	0.1 μg DDT/g oven dry solids				1.0 μg DDT/g oven dry solids				0.1 μg DDT/g oven dry solids				1.0 μg DDT/g oven dry solids			
	Components Removed in Sequential Extraction								Components Removed in Sequential Extraction							
EXTRACTABLE FRACTION	Untreated	Soluble salts	Organic matter	Iron oxides	Untreated	Soluble salts	Organic matter	Iron oxides	Untreated	Soluble salts	Organic matter	Iron oxides	Untreated	Soluble salts	Organic matter	Iron oxides
	labelled ^{14}C, % recovered															
water soluble	0.64, ±0.06	0.58 ±0.01	0.98 ±0.02	0.95 ±0.01	0.62 ±0.02	0.68 ±0.01	1.10 ±0.01	1.08 ±0.02	0.65 ±0.01	0.62 ±0.01	1.17 ±0.00	1.14 ±0.04	0.67 ±0.00	0.59 ±0.03	1.36 ±0.06	1.33 ±0.00
hexane:acetone extractable	27.3 ± 0.1	26.1 ± 1.2	46.7 ±12.4	41.2 ±15.5	21.2 ± 1.8	20.7 ± 5.0	73.1 ± 1.5	66.6 ± 9.6	41.1 ±16.4	60.9 ±16.6	75.6 ± 4.6	65.1 ±21.1	37.6 ± 6.5	27.6 ± 0.2	29.8 ± 5.2	31.5 ± 0.2

Mean quantity from extraction of duplicate subsamples

Standard deviation

in Calcasieu River and Mobile Bay sediment materials indicating the role of indigenous physical and chemical characteristics on the adsorption of DDT. The hexane-acetone extractable DDT in Calcasieu River sediment was less than found for Mobile Bay sediment material at 0.1 ppm, and at 1.0 ppm, the results were inconclusive. In general, the results suggest that among several components of sediments, organic matter appears to play a major role on the adsorption of DDT.

REDOX AND pH EFFECTS ON SETTLING RATE AND SOLID/LIQUID PHASE DISTRIBUTION OF ^{14}C-LABELLED DDT

Materials and Methods

The Mobile Bay sediment was incubated under reducing and oxidizing conditions at three pH (5.0, 6.5, and 8.0) levels for 3 months. The sediment was kept in suspension by continuous stirring. Nitrogen gas was bubbled through the suspensions to maintain reducing conditions. Oxygen gas was used to maintain oxidizing conditions. The pH of the sediment suspensions was controlled by adding either dilute hydrochloric acid or sodium hydroxide as necessary.

At the end of the 3-month incubation period, 300 ml of the preincubated sediment suspension was transferred to graduated cylinders containing 700 ml of distilled water. The pH of the distilled water in the graduated cylinder had been adjusted to correspond to the pH of the sediment suspensions.

One ml of the ^{14}C-labelled DDT (activity of 8.33 μCi/ml) was added to each of the graduated cylinders. All the suspensions were mixed thoroughly and allowed to settle. Suspension samples were withdrawn at 0.25, 0.5, 1, 2, 4, 8, 16, and 24 hours at the 700 ml level. (The cylinders were uniform with respect to height and diameter. Ten ml of the suspension was transferred to 40 ml centrifuge tubes containing 0.5 ml of NaCl solution (a flocculating agent). The suspensions were centrifuged for 15 minutes at about 1,000 RCF. The clear supernatant solution was transferred to glass vials. Addition of sodium chloride to aid in flocculation of suspended colloids and subsequent centrifugation was done instead of centrifugation and filtration because of the possibility the 0.45 μ membrane filters may retain some of the dissolved, labelled DDT by adsorption. After removing the water fraction, the residual sediment in the centrifuge tube was shaken for 30 minutes with 10 ml of a hexane-acetone mixture (3:1), centrifuged, and this supernatant extract transferred to glass vials. This fraction was called total although it is acknowledged labelled DDT recovery may not have been quantitative.

The sample solution was transferred to glass scintillation vials containing 15 ml of Aquasol scintillating liquid. The ^{14}C activity was determined by counting Beta radiation.

Results and Discussion

The suspension which was equilibrating under pH 8.0 oxidizing conditions was lost one night just a few days before this study was scheduled to be concluded due to abrasion from the magnetic stirrer bar and the sediment mineral phase which caused a hole to form in the bottom of the glass incubation flask.

Solvent-extractable, ^{14}C-labelled DDT thoroughly mixed with a Mobile Bay sediment-water mixture settled beneath the arbitrary sampling point (700 ml level on graduated cylinders) most rapidly under moderately acid (pH 5.0), reducing conditions during the 24 hour settling study (Table 7). Reducing, pH 8.0 conditions resulted in the maximum total levels (approximately 10 times pH 5.0, reducing levels) of labelled DDT at this sampling depth. Mildly alkaline conditions likely favored greater dispersion of colloidal materials which reduced flocculation and contributed to greater total levels in the upper part of the column relative to the more acid treatments. Soluble levels also were slightly greater under pH 8.0, reducing conditions (Table 8). If the increase in soluble levels with increasing pH is real, it is likely due to: 1) an equilibrium with the greater total levels or 2) the effects of increasing pH on increasing the concentration of soluble humic acids which may complex with DDT.

Because of interactions imposed between physicochemical, treatments, time, particle size distribution, equilibrium between solid and soluble forms, the loss of the pH 8.0 oxidizing treatment, and some experimental error, the results of this study were difficult to evaluate. There was some suggestion that under reducing conditions for the Mobile Bay sediment, moderately acid conditions would tend to effect more rapid removal of soluble and especially suspended particulate DDT forms from a quiescent water column than near neutral or slightly alkaline pH conditions.

REDOX AND pH EFFECTS ON DIFFUSION OF DDT AND KEPONE INTO SEDIMENT CORES

Materials and Methods

A quantity of Mobile Bay sediment was added to six 4-liter Erlenmeyer flasks containing deionized water at a solid:solution ratio of 1:4. The sediment material was incubated under three different pH (5, 6.5 and 8.0) and two different redox conditions

TABLE 7. THE ACTIVITY OF 3:1 HEXANE:ACETONE EXTRACTABLE ^{14}C-LABELLED DDT WITH TIME IN COLUMN SETTLING STUDIES

Settling time, hours	Reduced Sediment			Oxidized Sediment	
	pH 5.0	pH 6.5	pH 8.0	pH 5.0	pH 6.5
	------- counts per minute/10 ml sample -------				
0.25	7,480	8,010	12,620	7,449	4,928
0.5	6,127	6,591	13,080	6,650	2,903
1	7,007	7,244	8,961	6,280	2,898
2	2,128	7,112	6,116	797	388
4	1,207	6,816	3,911	700	298
8	119	5,870	1,624	295	130
16	77	1,957	1,023	298	175
24	64	353	652	105	102

TABLE 8. THE ACTIVITY OF WATER SOLUBLE ^{14}C-LABELLED DDT WITH TIME IN COLUMN SETTLING STUDIES

Settling time, hours	Reduced Sediment			Oxidized Sediment	
	pH 5.0	pH 6.5	pH 8.0	pH 5.0	pH 6.5
	------- counts per minute/10 ml sample -------				
0.25	113	447	430	1137	186
0.5	89	380	312	276	123
1	64	221	483	226	199
2	68	127	385	99	69
4	43	95	127	55	37
8	29	90	91	55	32
16	23	193	93	57	70
24	24	80	94	65	48

for 90 days so that both the chemical and biological systems reach equilibrium.

At the end of the 3-month incubation period, moisture contents of the sediment suspensions were determined. Then, a calculated quantity of the incubated sediment suspensions was transferred to glass cylinders which were sealed at the bottom. The sediment suspensions were allowed to settle for two days. Approximately 500 grams of sediment material (oven dry solids) were present in each cylinder.

A coarse textured soil was combusted at 1000°C and spiked at a level of 1,000 μg/g DDT and Kepone. Five grams of this spiked soil was added to the flood water in each cylinder, and allowed to settle to the sediment water interface. The cylinders containing the sediments spiked with DDT and Kepone were kept in a dark room at 27°C for six months. The flood water lost by evaporation was replaced frequently with deionized water.

At the end of the 6-month incubation period, the sediment in the glass cylinder was frozen and sectioned at 1-cm intervals. The sediment in each section was dried in draft oven at 40°C, and analyzed for DDT and Kepone which diffused from the surface into deeper layers.

The pH 8.0, oxidizing suspension was lost just before the 90-day equilibration period ended as discussed elsewhere. The pH 5.0, reduced Kepone column was broken.

Results and Discussion

Table 9 gives DDT and Kepone levels vs depth in the column diffusion studies. No clear treatment effects were apparent and sampling problems made critical evaluation of this data of dubious value. The initial horizon of each core consisted of a thin layer of 0.5 to about 1.2 cm thick which was poorly consolidated compared to lower horizons. In the initially reduced cores, this poorly consolidated layer was approximately the same thickness as the surface oxidized sediment layer as indicated by the light brown color of this surface horizon. An attempt was made to keep the thickness of subsequent horizons a uniform 1.5 cm, though this may have varied slightly. Because of possible problems in obtaining uniform depth increments in each column, these data are presented with no interpretation or conclusions attempted.

TABLE 9. DIFFUSION OF DDT AND KEPONE FROM A SEDIMENT-WATER INTERFACE INTO MOBILE BAY SEDIMENT MATERIAL EQUILIBRATED UNDER A RANGE OF pH AND REDOX POTENTIAL CONDITIONS

	DDT, µg/g oven dry solids					
	Reducing			Oxidizing		
Horizon	pH 5.0	pH 6.5	pH 8.0	pH 5.0	pH 6.5	pH 8.0
1	902	1260	450	590	619	†
2	26.8	1.3	2.4	33.5	4.6	
3	1.70	0.12	0.50	0.25	0.08	
4	0.22	0.10	0.57	¶	0.06	
5	0.17	0.05	0.11	¶	¶	

	Kepone, µg/g oven dry solids					
	Reducing			Oxidizing		
Horizon	pH 5.0	pH 6.5	pH 8.0	pH 5.0	pH 6.5	pH 8.0
1	‡	182	364	209	207	†
2		35.6	57.9	42.0	70.6	
3		1.65	5.96	0.89	1.15	
4		0.21	0.06	0.02	0.05	
5		0.02	0.04	¶	¶	

[†] Sediment suspension lost during preincubation

[¶] Lost sample

[‡] Core column broke

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APPENDIX A

DEVELOPMENT AND TESTING OF PROCEDURES/TROUBLE SHOOTING/ADDITIONAL NOTES/QUALITY ASSURANCE

INTRODUCTION

The previous sections of this report represent work conducted to meet research objectives. A considerable amount of additional work was performed in testing and developing procedures, trouble shooting, and repeating studies with which there were problems. This section will briefly discuss some of this work. The objectives of this section are to: 1) present information and procedures which may be useful to others initiating pesticide research in sediment-water systems, 2) present findings of studies to determine the recovery efficiency of extraction methods used for the primary degradation experiments, and 3) provide additional information on the conduct of this project, such as the need to repeat some work and substantially modify procedures on some studies.

TESTING OF EXTRACTION METHODS

DDT

In addition to surveying the literature for extraction methods for DDT, four local and regional laboratories conducting pesticide monitoring or research were visited to obtain information on methodology. These were: Feed and Fertilizer Laboratory, Louisiana State University campus; laboratory of the Louisiana Wildlife and Fisheries Commission, Division of Water Pollution Control, Louisiana State University campus; USDA Soil and Water Pollution Laboratory, Baton Rouge, Louisiana; and the Pesticides Monitoring Laboratory, U.S. EPA. Bay St. Louis, Mississippi.

Initial experience with the commonly used method of shaking soil or sediment samples with appropriate organic solvents to extract DDT was not satisfactory with the Mobile Bay sediment material. It was soon apparent that good and reproducible recovery of DDT from fine textured, anaerobic sediments was more difficult to achieve than from typical agricultural soils. A 12-hour Soxhlet extraction using 3:1 hexane-acetone gave recoveries consistently between 90 and 95 percent on Mobile Bay sediment suspensions which had been incubated under weakly reduced to well oxidized conditions. Recovery from spiked, strongly reduced samples were not as good and tended to be less reproducible. The reasons for this difficulty were not readily apparent. At first it was believed that drying of anaerobic wet sediment samples in a draft oven at 35-40°C for 1 to 3 days may have contributed a drying artifact and alternate sample drying procedures were developed (see Acetone Drying of Wet Sediment Samples, page 74). However, results using alternate drying methods and reevaluation of the data suggested any apparent improvement in DDT recovery from strongly reduced sediments was probably more a function of how quickly the spiked test suspensions were extracted rather than any improvement resulting from modified drying procedures. It was not possible to quantify the recovery efficiency for DDT from the strongly reduced Mobile Bay sediment suspensions because, as discussed elsewhere in this report, there was evidence that some of the DDT degraded very rapidly under strongly reduced conditions in addition to any other processes which may have affected extractable DDT levels.

Kepone

Recovery of Kepone from James River sediment material was initially tested using the same extraction method applied to Mobile Bay sediments for DDT as well as two other solvent systems (Table A-1).

When routine extraction and analysis of Kepone samples from the controlled pH-redox potential studies were begun, it was soon apparent that Kepone extraction efficiency was poorly reproducible. At this time we became aware of a 1977 publication by Moseman et al. (69) on Kepone methodology in which the benzene-methanol solvent system was found to give good recovery of Kepone and to aid in obtaining reproducible electron capture response compared to other extracting solvents. These procedures were tested on Kepone-amended James River sediment suspensions and were found to give fair to good recovery and good reproducibility. Subsequently, we switched to the benzene-methanol procedure and repeated earlier studies done with hexane-acetone.

Permethrin

This laboratory's experience with DDT and Kepone indicated good and reproducible pesticide extraction from fine grained, anaerobic sediments was more difficult than extraction from typical aerobic agricultural soils for which most published extraction methods have been used. Therefore, a thorough study of various extraction procedures was conducted on both oxidized and reduced soil amended with Permethrin before initiating experimental incubations under controlled pH and oxidation-reduction conditions.

TABLE A-1. KEPONE RECOVERY FROM AMENDED JAMES RIVER SEDIMENT SUSPENSIONS†

Solvent System	Drying Procedure	Suspension Treatment	
		Oxidized	Reduced
		---- Recovery, % ----	
1:1 hexane-acetone	35°C, draft oven	20	10
1:5 methylenechloride-hexane	35°C, draft oven	20	10
3:1 hexane-acetone	35°C, draft oven	72	14
3:1 hexane-acetone	acetone¶	72	100

†12-hour Soxhlet extraction

¶see Acetone Drying of Wet Sediment Samples

A summary of the methods tested for extracting Permethrin from wet soil samples is given below. The excess water initially present in the sample was removed by centrifugation, extracted, and analyzed for Permethrin. It was found that essentially all of the Permethrin added to the soil-water mixtures was partitioned with the solid phase as essentially no Permethrin was measured in the aqueous phase.

Permethrin recovery by the various extraction methods tested are given in Table A-2 for both oxidized and reduced soil samples. The 1.5:1 hexane-acetone solvent system with 8-hour Soxhlet extraction method was selected and used for all Permethrin work (see Table A-3).

ACETONE DRYING OF WET SEDIMENT SAMPLES

During initial DDT degradation studies, recovery of DDT from strongly reduced sediment samples was well below levels added to the suspensions, even after only a few hours to one day following DDT amendments. Elevated levels of degradation products were also apparent only a few hours to 1 day into the incubation. At the time, these rapidly occurring transformations of DDT were interpreted as changes occurring during the drying step for the strongly reduced samples which appeared as treatment effects.

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TABLE A-2. SUMMARY OF METHODS TESTED FOR EXTRACTING PERMETHRIN FROM OXIDIZED AND REDUCED SOIL SUSPENSIONS

I. Acetone Drying Method[†]

- A. 4-hour Soxhlet extraction
  - 1. 1:1 hexane-acetone
  - 2. 1:2 hexane-methanol
- B. 12-hour Soxhlet extraction
  - 1. 1:1 hexane-acetone
  - 2. 1:2 hexane-methanol
- C. 8-hour Soxhlet extraction[¶]
  - 1. 1.5:1 hexane-acetone

II. Oven Drying (40°C for 48 hours)

- A. 4-hour Soxhlet extraction
  - 1. 1:1 hexane-acetone
  - 2. 100% hexane
- B. 12-hour Soxhlet extraction
  - 1. 1:1 hexane-acetone
  - 2. 100% hexane

III. Shaking Moist Samples with Extracting Solvent

- A. Methanol extraction[‡]
- B. 1:1 hexane-acetone extraction[ε]

[†] See Acetone Drying of Wet Sediment Samples

[¶] Permethrin method used by U.S.D.A. Soil and Water Pollution Laboratory, Baton Rouge, Louisiana

[‡] Two grams soil + 5 grams NaCl shaken for 30 minutes with 9:1 methanol-water mixture. Mixture was filtered, extracted three times with methylene chloride, the methylene chloride concentrated on hot plate, 100 ml hexane added, and solvent system again concentrated on hot plate to 50 ml, then dried by eluting through Na_2SO_4

[ε] Two grams soil + 5 grams NaCl shaken with 100 ml of 1:1 hexane-acetone for 30 minutes, filtered, acetone extracted with water and hexane solution dried with Na_2SO_4

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TABLE A-3. PERMETHRIN RECOVERY FROM SPIKED OXIDIZED AND REDUCED SOIL SUSPENSIONS BY VARIOUS EXTRACTION METHODS

Extraction Method	Recovery, %	
	Oxidized	Reduced
acetone dry, 4-hr Soxhlet, 1:1 hexane-acetone	78	58
acetone, 4-hr Soxhlet, 1:2 hexane-methanol	67	60
acetone dry, 12-hr Soxhlet, 1:1 hexane-acetone	76	82
acetone dry, 12-hr Soxhlet, 1:2 hexane-methanol	95	89
acetone dry, 8-hr Soxhlet, 1.5:1 hexane-acetone	90	90
oven dry, 4-hr Soxhlet, 1:1 hexane-acetone	66	76
oven dry, 4-hr Soxhlet, 100% hexane	88	63
oven dry, 12-hr Soxhlet, 1:1 hexane-acetone	58	61
oven dry, 12-hr Soxhlet, 100% hexane	71	75
methanol extraction of moist soil by shaking	64	74
1:1 hexane-acetone extraction of moist soil by shaking	79	74

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The original procedure used for reduced samples had been to remove excess water from the sediment-water mixtures by centrifugation and then dry the wet sediment samples at 35°C in a forced draft oven. This temperature range was found to give good recovery from oxidized sediment samples whereas higher oven temperatures resulted in poor DDT recovery, presumably due to volatilization losses. However, the low drying temperature necessitated 1 to 4 days in the oven, depending on sample size. It was believed the exposure of strongly reduced sediments to oxidized conditions near the optimum temperatures for most microbial activity may have favored an enhanced rate of chemical degradation or mixed anaerobic-aerobic microbial activity which was not typical of sediment-water systems.

Although Browman (70) reported successful extraction of wet (moisture remaining after pouring off excess water) sediments by shaking with organic solvents, preliminary studies indicated shaking was not a satisfactory method for our samples. Soxhlet extraction of wet sediments was also not satisfactory. Thus sediment drying seemed an essential step.

A number of different drying techniques were examined including freeze drying. The most satisfactory technique was to centrifuge the sediment-water mixtures and decant the supernatent water as before, then remove the residual moisture by shaking the solids with acetone twice, evaporating residual acetone under a nitrogen stream, and combining the DDT extracted during the acetone drying step with the solvent mixture from the Soxhlet extraction of the solid phase. The samples can be dried in less than 2 hours using this procedure. This method was tested on reduced sediment suspensions and recovery approached 80 percent vs greater than 90 percent for oxidized samples.

Surprisingly, extracted levels of DDT in the most strongly reduced samples at each pH was again found to be far below spiking levels within a very short time. The apparent high recovery efficiency of the extraction procedure using acetone drying and the continued low DDT/high DDD levels in the early portion of the experimental incubations under controlled physicochemical conditions probably resulted from sampling and extraction of the acetone drying test samples about 1 hour after spiking which gave less time for microbial or chemical decomposition in the reduced suspension.

REMOVAL OF SULFUR INTERFERENCE FROM SOLVENT EXTRACTS OF STRONGLY REDUCED SOIL AND SEDIMENT SAMPLES

Organic solvent extraction of certain strongly reduced soils and sediments will solubilize sufficient sulfur to contaminate the column and/or electron capture detector for a considerable period of time masking pesticide peaks. Many of the reduced Mobile Bay sediment extracts required treatment to remove sulfur. This was done by treating bare, 12 gauge copper wire with 4N HNO_3 to remove oxide coatings and immersing the surface active wire in the sample test tubes for about 30 minutes with occasional swirling. More than one treatment was sometimes necessary to remove the sulfur. This method was a modification of a published procedure (67). A small quantity of elemental mercury can be added to the sample as an alternate way of removing sulfur interference.

A PROBLEM WITH ERRATIC RESPONSE OF GAS CHROMATOGRAPH TO KEPONE SAMPLES AND STANDARDS

Kepone was being analyzed with a 1.5 percent OV-1, 1.95 percent QF-1 column connected to an electron capture detector. For the first few months of Kepone analyses, the instrument response (peak height or peak area) was reproducible to within 4 percent and usually within 2 percent on repeated injections of the same sample or standard.

Over a very short period of time, the response became erratic and varied from 20 to as much as 40 percent on repeated sample or standard injections. The instrument electronics were determined to be stable. The usual cleanup procedures of replacing the silanized glass wool packing at the beginning of the column and solvent rinsing plus high temperature "baking out" of the injector and interface tubing did not alleviate the problem. It was noted that where standards containing both Aldrin and Kepone were injected repeatedly, the Aldrin response was very reproducible and the Kepone response was not.

This erratic response to Kepone was confirmed on two other electron capture instruments at the USDA Soil and Water Pollution Control Laboratory in Baton Rouge. Thus the problem appeared peculiar to Kepone. A telephone conversation with personnel of the USDA Plant Protection Laboratory at Gulfport Mississippi who were experienced with Kepone analysis revealed that this is not an uncommon problem with Kepone. This lab often derivatized the Kepone in samples to overcome poor gas chromatography performance for Kepone.

While getting set up to do the same with our Kepone samples, it was learned that, by mistake, someone had ammended the sediment suspensions used for one short term auxiliary Kepone study with 100 μg/g levels of Zn, Cu, Cd, and Pb.

It seemed plausible that the hot benzene-methanol extract was removing a portion of these metals which accumulated as a solid residue in the glass liner of the injector. These residual metal deposits may have catalyzed some Kepone decomposition within the injector resulting in a highly variable response. The glass injector liners were cleaned by repeated rinsing with 4N nitric acid (a common method of removing metal contamination from glassware). This treatment was successful in restoring the gas chromatograph to give a stable and reproducible response to Kepone.

It is possible that solvent extraction of indigenous metals from soils and sediments would eventually cause the same problem with Kepone in many instruments.

After this incident, the glass injector liners were periodically acid cleaned and no further problems developed with the Kepone analyses.

REPEATED STUDIES

DDT

Because we initially believed the DDT sample processing methods for strongly reduced sediments were contributing to drying artifacts, new drying methods were implemented (see Acetone Drying for Wet Sediment Samples, page 74) and incubations were repeated for the -150 and 50 mv treatments at all three pH levels using a somewhat greater sampling frequency. The repeated data are presented in this report due to the greater sampling frequency and less apparent experimental error at pH 6.0. This accounts for the different sampling dates on oxidized and reduced treatments.

The repeated work showed the low initial recovery of DDT from strongly reduced samples was apparently not a drying artifact as discussed elsewhere in this report. In most cases the data from repeated studies was very similar to the original data.

Kepone

A Kepone incubation at pH 6.5 was completed using a hexane-acetone extractant and samples were stored. Another incubation at pH 8.0 was in progress before a problem with extracting methods was detected. Extraction and analyses for Kepone were stopped until the procedure was changed giving good and reproducible Kepone recovery. Thus the pH 8.0 study data begins on sampling day 16 where a benzene-methanol extraction procedure was implemented. The data for pH 6.5 using hexane-acetone was not included in this report. Instead, this study was repeated at pH 7.0 using the benzene-methanol procedure.

QUALITY ASSURANCE

The number of sample processing steps for each pesticide analysis in this study was large (page 25, 28, and 29). Many of these steps were necessary to remove the water from the suspension aliquots taken for samples. This is in contrast to most residue analysis procedures which start with an air-dried soil. The large number of steps introduces considerable opportunity for experimental error to creep into the methodology.

For most of the analyses for pesticide recovery under controlled physicochemical conditions, duplicate sample aliquots were withdrawn, and were processed and analyzed by gas chromatography separately. These duplicate analyses are indicated in Figures 3, 4, 6, 7, 9, 10, 11, 12, 13, 14, 15, and 16 where two data points are given for each sampling date. The precision of the extraction procedure as indicated by the closeness of duplicate values on separate sample aliquots appeared very good in most cases.

Accuracy is indicated by comparing recovery levels at the first sampling date in an incubation with the spiking levels presented in the legend for each of Figures 2-16. With a few exceptions which are apparent in the figures, the ability to recover spiking levels was satisfactory. The low initial recoveries of DDT under strongly reducing conditions (-150 mv) was believed due to rapid degradation, and this is examined more thoroughly in the DDT discussions.

Replication refers to data obtained from individual experimental units. The duplicate values discussed above to illustrate the precision of the sample processing procedure represent subsampling, not replication. The degradation studies under controlled pH and redox potentials (Figures 2-16) were subsampled, but not replicated. It was believed our experimental objectives, with the time and equipment available, would best be served by having a larger number of treatments (where treatments were different levels of a continuous variable) with a large number of samples taken with time. However, the question of reproducibility of experimental results (treatment effects) needs to be addressed. The repeated studies done with DDT under reduced conditions do approximate replication. Recall that many of the incubations of DDT at -150 and 50 mv were repeated at a later date using a different sample drying procedure. As reported elsewhere, it was eventually concluded that the method of drying did not account for the rapid decrease in DDT levels at -150 mv. Thus the repeated studies represent samples taken at different times from different microcosms incubated under the same imposed physicochemical conditions. Figure A-1 illustrates the recovery of DDT with time at pH 8.0 and +50 mv from two different incubations. A redox potential of 50 mv was selected for

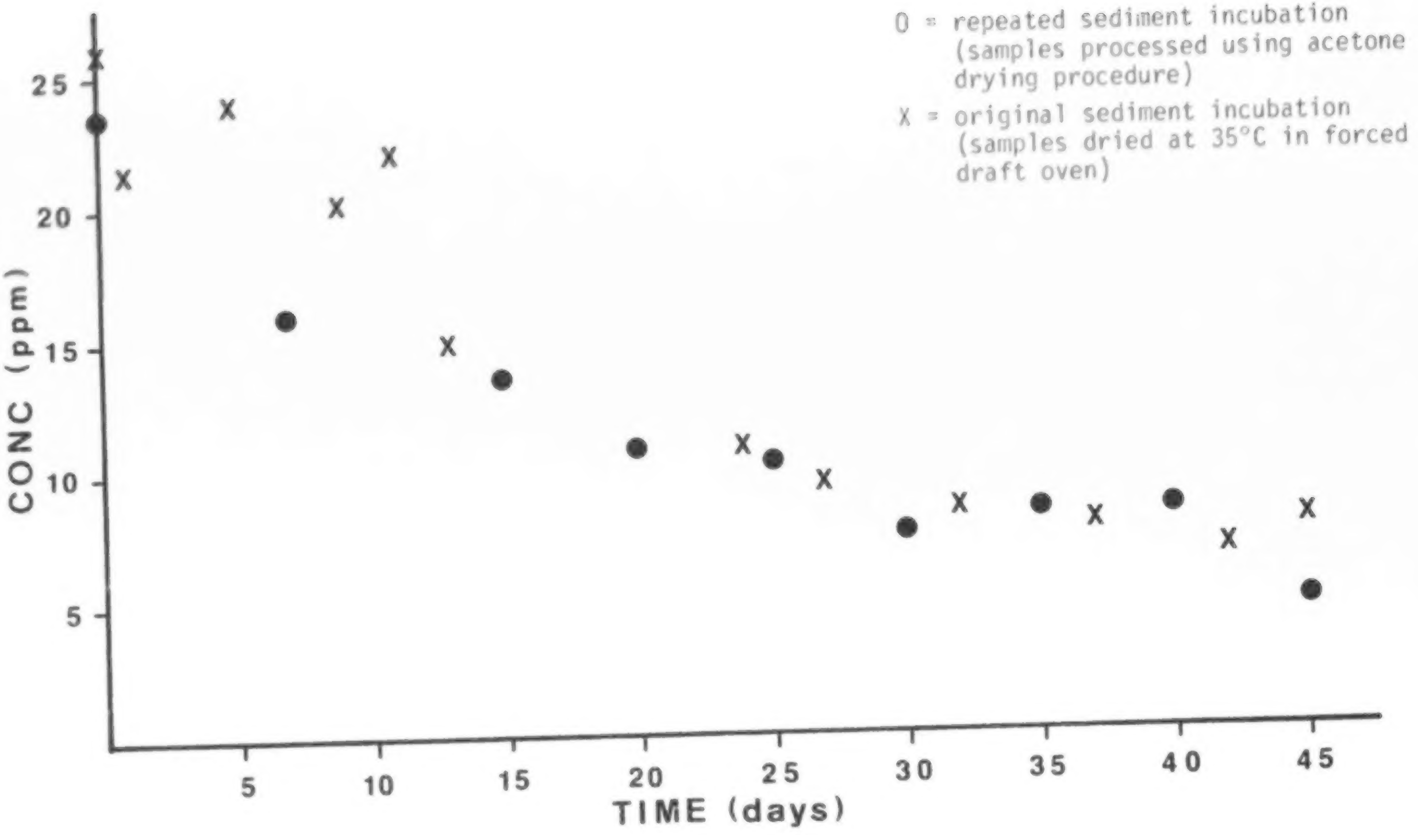

Figure A-1: DDT Recovery with Time from Two Mobile Bay Sediment Suspensions Incubated at pH 8.0 and +50 mv.

comparisons because at this potential there was a moderate decrease in recovery throughout the incubation. Other than some scatter seen in data points during the first few days of the original incubation, DDT levels and changes in DDT levels were very similar from the two microcosms. This is an indication that the microcosms do replicate reasonably well.

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APPENDIX B. TABLES FOR DDT, KEPONE, AND PERMETHRIN DEGRADATION STUDIES UNDER CONTROLLED pH AND REDOX POTENTIAL CONDITIONS

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TABLE B-1. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED DDT DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 6.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	------- DDT, µg/g oven dry solids -------			
0	22.0[†]	[¶]	[¶]	24.0
1	6.6	24.2	21.5	24.0
2	1.3	21.9		
3	0.8	20.8		
4	0.4	19.6	23.3	17.4
5	0.6	22.3		
7	0.4	20.6	17.5	22.7
9	0.2	21.3		
10			20.4	19.9
11	0.4	12.6		
13	0.5	14.2		
15	0.3	17.9	16.2	16.7
18	0.7	16.9		
20			16.9	13.1
21	1.7	10.4		
24	0.6	11.8		
25			14.0	14.8
30			17.0	16.0
32	0.2	11.3		
35			13.1	12.2
37	0.0	14.4		
40			18.5	17.0
42				
45	0.1	10.4	14.0	16.0

[†] Quantity from extraction of single sample

[¶] Lost sample/missing value

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TABLE B-2. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED DDT DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 7.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	DDT, μg/g oven dry solids			
0	†	34.8[¶]		
1	10.3	27.4	25.9[‡]	40.8[ε] ± 5.0[ϕ]
4	5.1	23.2	54.6 ± 2.7	38.1 ± 6.4
5	2.6	30.8		
7	1.7	26.5	22.8 ± 0.6	27.0 ± 2.5
9	†	29.4		
11	3.1	27.1		
12			25.2 ± 0.9	28.6 ± 1.2
13	0.8	19.3		
18	0.1	14.8		
19			18.4 ± 4.0	15.0 ± 1.4
21	†	†		
22			21.7 ± 1.3	22.6 ± 0.4
24	†	†		
27	0.1	8.3		
28			22.4 ± 0.0	23.0 ± 0.9
32	0.0	9.5	†	20.6 ± 0.2
36			†	
37	†	10.2		
41			17.0 ± 0.7	20.6[‡]
42	†	7.6		
45	0.0	†		

[†] Lost sample/missing value

[¶] Quantity from extraction of single sample

[‡] Lost one subsample

[ε] Mean quantity from extraction of duplicate subsamples

[ϕ] Standard deviation

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TABLE B-3. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED DDT DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 8.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	------ DDT, μg/g oven dry solids ------			
0	2.5[†] ±0.0[¶]	23.4	27.2 ± 0.0	25.4 ± 0.8
1	2.4 ±0.1	‡		
4	1.0 ±0.0	‡		
7	0.0 ±0.0	15.8 ± 0.1	23.2 ± 0.0	25.8 ± 0.6
15	0.4 ±0.0	13.5 ± 0.0	17.7 ± 0.1	17.2 ± 1.1
20	0.2 ±0.0	11.6 ± 0.9	18.0 ± 0.1	16.6 ± 1.2
25	‡	10.1 ± 0.0	15.2 ± 1.3	15.8 ± 0.2
30	0.0 ±0.0	7.5 ± 0.0	15.8 ± 0.2	17.8 ± 0,2
35	‡	8.2 ± 0.0	13.6 ± 0.1	15.3 ± 0.4
40	0.0 ±0.0	8.2 ± 0.4	16.0 ± 0.3	16.3 ± 0.6
45	0.0[ε]	4.7 ± 0.1	13.7 ± 0.6	14.2 ± 0.3

[†] Mean quantity from extraction of duplicate subsamples

[¶] Standard deviation

[‡] Lost sample/missing value

[ε] Lost one subsample

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TABLE B-4. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDD DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 6.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	-------- DDD, μg/g oven dry solids --------			
0	1.37[†]	[¶]	0.57	0.63
1	5.93	0.67	0.73	0.67
2	6.70	0.57		
3	6.60	0.47		
4	4.75	1.05	0.57	0.73
5	6.17	0.65		
7	5.42	0.75	[¶]	0.87
9	5.50	0.75		
10			0.55	0.47
11	4.80	1.03		
13	4.50	0.73		
15	4.42	0.83	1.00	0.37
18	4.55	0.87		
20			0.45	0.27
21	3.55	1.35		
24	2.55	0.70		
25			0.52	0.50
30			0.69	1.00
32	2.22	0.69		
35			0.79	0.67
37	2.45	0.69		
40			0.61	0.61
42				
45	2.37	1.00	0.61	0.46

[†] Quantity from extraction of single sample

[¶] Lost sample/missing value

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TABLE B-5. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDD DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 7.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	------- DDD, μg/g oven dry solids -------			
0	[†]	1.01[¶]		
1	1.86	0.98	0.70[‡] ±0.31[ε]	0.38 ±0.09
4	8.07	0.94	0.30 ±0.04	0.45 ±0.13
5	5.07	1.10		
7	4.60	1.25		
9	1.10	0.16		
11	1.78	1.14		
12			0.34 ±0.01	0.24 ±0.02
13	1.27	1.16		
18	1.32	0.15		
19				
21	2.29	1.45		
22				
24	2.99	2.14		
27	2.07	1.07		
28			0.33 ±0.07	0.27 ±0.00
32	2.22	1.30		
36				
37	2.37	1.30		
41			0.28 ±0.04	0.24 ±0.02
42	2.14	1.16		
45	2.37	1.38		

[†] Lost sample/missing value

[¶] Quantity from extraction of single sample

[‡] Mean quantity from extraction of duplicate subsamples

[ε] Standard deviation

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TABLE B-6. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDD DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 8.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	------ DDD, μg/g oven dry solids ------			
0	7.62[†] ±0.24[¶]	0.71 ±0.15	0.64 ±0.02	0.56 ±0.09
1	6.28 ±0.23	[‡]	[‡]	[‡]
4	6.41 ±0.06	[‡]	[‡]	[‡]
7	6.91 ±0.10	1.56 ±0.05	0.59 ±0.00	0.45 ±0.04
15	5.24 ±0.13	1.28 ±0.08	0.80 ±0.32	0.56 ±0.07
20	4.26 ±0.13	1.41 ±0.03	0.64 ±0.02	0.54 ±0.07
25	3.66 ±0.15	1.94 ±0.91	0.62 ±0.01	0.48 ±0.12
30	4.64 ±0.06	2.04 ±0.02	0.61 ±0.03	0.44 ±0.02
35	2.90 ±0.06	1.46 ±0.02	0.64 ±0.03	0.41 ±0.04
40	3.06 ±0.11	1.88 ±0.06	0.92 ±0.04	0.40 ±0.04
45	2.96 ±0.03	2.07 ±0.35	0.68 ±0.16	0.37 ±0.07

[†] Mean quantity from extraction of duplicate subsamples

[‡] Lost sample/missing value

[¶] Standard deviation

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TABLE B-7. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDE DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 6.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	------- DDE, μg/g oven dry solids -------			
0	0.25[†]	[¶]	0.27	0.30
1	0.95	[¶]	0.25	0.32
2	0.95	0.12		
3	0.95	0.12		
4			0.12	0.12
5	0.87	0.15		
7	0.75	0.15	0.17	0.20
9	0.83	0.15		
10			0.17	0.15
11	0.65	0.12		
13	0.70	0.15		
15	0.63	0.17	0.17	0.13
18	0.67	0.20		
20			0.12	0.12
21	0.45	0.12		
24	0.35	0.17		
25			0.15	0.17
30				
32	0.35	0.07		
35				
37	0.34	[¶]		
40				
42	[¶]	0.24		
45	0.32	0.63		

[†] Quantity from extraction of single sample

[¶] Lost sample/missing value

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TABLE B-8. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDE DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 7.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	DDE, µg/g oven dry solids			
0	[†]	0.45[¶]		
1	0.34	0.39	0.08[‡] ±0.12[ε]	0.11 ±0.08
4	0.92		0.00 ±0.00	0.04 ±0.01
5	0.81	0.37		
7	0.75	0.32		
9	0.68	0.09		
11	0.68	0.41		
12			0.06 ±0.01	0.08 ±0.01
13	0.54	0.18		
18	0.21	0.20		
19				
21	0.38	0.99		
22				
24	0.36	0.84		
27	0.63	0.70		
28			0.08 ±0.01	0.12 ±0.01
32	0.37	0.81		
36				
37	0.39	0.74		
41			0.06 ±0.04	0.08 ±0.01
42	0.36	0.71		
45	0.38	0.83		

[†] Lost sample/missing value

[¶] Quantity from extraction of a single sample

[‡] Mean quantity from extraction of duplicate subsamples

[ε] Standard deviation

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TABLE B-9. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF DDE DURING A 45-DAY INCUBATION OF MOBILE BAY SEDIMENT SUSPENSION AT pH 8.0

Incubation Period, days	Redox Potential, mv -150	50	250	450
	------ DDE, μg/g oven dry solids ------			
0	0.96[†] ±0.02[‡]	0.18[¶]	0.26 ±0.04	0.34 ±0.07
1	[ε]	[ε]	[ε]	[ε]
4	0.96 ±0.01	[ε]	[ε]	[ε]
7	0.94 ±0.04	0.34 ±0.00	0.27 ±0.01	0.19 ±0.01
15	0.69 ±0.06	0.28 ±0.03	0.33 ±0.05	0.29 ±0.00
20	0.58 ±0.02	0.30 ±0.04	0.29 ±0.03	0.27 ±0.02
25	0.56 ±0.04	[ε]	0.30 ±0.01	0.27 ±0.01
30	0.54 ±0.02	0.38 ±0.01	0.37 ±0.00	0.26 ±0.02
35	0.38 ±0.12	[ε]	0.37 ±0.05	0.30 ±0.07
40	0.54 ±0.01	0.31 ±0.01	0.38 ±0.02	0.28 ±0.01
45	0.44 ±0.02	0.34[¶]	0.39[¶]	0.34[¶]

[†] Mean quantity from extraction of duplicate subsamples

[¶] Lost one subsample

[‡] Standard deviation

[ε] Lost sample/missing value

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TABLE B-10. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED KEPONE DURING A 51-DAY INCUBATION OF JAMES RIVER SEDIMENT SUSPENSION AT pH 5.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	----- Kepone, μg/g oven dry solids -----			
0	17.6[†] ± 0.8[¶]	18.6 ± 0.2	17.8 ± 0.5	14.7 ± 0.5
1	16.8 ± 0.6	17.8 ± 0.7	17.7 ± 0.2	15.5 ± 0.1
2	18.0 ± 0.8	20.6 ± 3.0	16.5 ± 2.4	16.0 ± 0.7
4	14.3 ± 0.3	17.4 ± 0.1	15.6 ± 0.4	14.8 ± 0.4
6	15.2 ± 2.4	16.1 ± 0.1	18.2 ± 0.5	13.7 ± 1.3
9	15.5 ± 0.2	17.9 ± 0.2	15.8 ± 1.2	15.6 ± 1.6
12	14.9 ± 3.8	17.3 ± 2.6	16.8 ± 0.8	13.4 ± 1.6
15	15.0 ± 0.2	16.4 ± 0.3	13.0 ± 0.8	12.3 ± 0.8
18	13.9 ± 0.8	11.7 ± 1.7	13.4 ± 0.4	12.8 ± 0.9
24	13.2 ± 0.5	14.1 ± 1.3	13.3 ± 0.9	9.7 ± 0.0
27	17.3 ± 0.2	15.7 ± 0.0	16.2 ± 1.4	16.4 ± 0.2
35	‡	‡	‡	‡
45	12.2 ± 0.1	13.6[c]	16.1 ± 0.8	13.9[c]
51	17.7[c]	12.6 ± 0.6	13.6 ± 0.9	12.4 ± 0.4

[†] Mean quantity from extraction of duplicate subsamples

[¶] Standard deviation

[‡] Lost sample/missing value

[c] Lost one subsample

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TABLE B-11. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED KEPONE DURING A 52-DAY INCUBATION OF JAMES RIVER SEDIMENT SUSPENSION AT pH 7.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	----- Kepone, µg/g oven dry solids -----			
0	19.7[†] ± 0.5[¶]	20.0 ± 0.5	17.3 ± 3.6	17.6 ± 0.8
1	22.1 ± 0.0	18.0 ± 0.7	19.6 ± 1.1	17.9 ± 5.0
2	16.7 ± 1.4	18.6 ± 0.0	20.3 ± 1.1	20.6 ± 1.6
4	21.0 ± 0.0	16.4 ± 1.7	20.7 ± 2.4	19.0 ± 0.4
6	18.5 ± 1.8	17.3 ± 0.5	20.1 ± 0.6	18.6 ± 0.7
9	20.9 ± 1.2	20.1 ± 1.8	17.3 ± 0.4	19.9 ± 4.8
15	17.1 ± 2.7	16.8 ± 0.0	18.2 ± 1.4	19.9 ± 0.6
18	18.9 ± 0.5	18.2 ± 0.4	20.3 ± 1.8	19.5 ± 1.5
21	18.7 ± 0.9	18.9 ± 0.8	18.9 ± 0.8	19.4 ± 0.9
24	15.7 ± 0.7	15.9 ± 0.2	16.1 ± 0.5	16.5 ± 0.3
27	16.6 ± 1.4	14.7 ± 0.4	18.4 ± 0.4	16.7 ± 2.0
30	16.0 ± 1.6	14.0 ± 1.7	19.8 ± 0.8	19.6
35	19.3 ± 0.9	19.8 ± 0.2	21.2 ± 0.2	19.0 ± 2.0
40	19.3 ± 4.7	20.5 ± 2.1	20.8 ± 5.2	13.6 ± 3.7
45	20.6 ± 0.4	19.7 ± 0.1	18.2 ± 0.2	17.0 ± 0.6
52	18.9 ± 3.7	22.4 ± 0.3	22.1 ± 1.3	19.8 ± 2.5

[†] Mean quantity from extractions of duplicate subsamples

[¶] Standard deviation

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TABLE B-12. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED KEPONE DURING A 70-DAY INCUBATION OF JAMES RIVER SEDIMENT SUSPENSION AT pH 8.0

Incubation Period, days	Redox Potential, mv -150	 50	 250	 450
	------ Kepone, µg/g oven dry solids ------			
16	22.0[†] ± 1.2[¶]	20.4 ± 1.1	20.0 ± 5.8	20.3 ± 2.2
19	17.8 ± 2.1	17.5 ± 0.7	17.8 ± 1.7	16.8 ± 0.3
24	21.6 ± 0.4	23.0 ± 4.0	19.4 ± 5.3	18.4 ± 0.3
30	21.4 ± 1.5	19.9 ± 0.5	17.2 ± 0.1	17.3 ± 1.8
37	21.7 ± 0.6	19.7 ± 1.9	22.3 ± 2.0	19.8 ± 3.8
42	21.0 ± 0.8	18.5 ± 0.6	18.2 ± 3.1	20.9 ± 4.0
49	17.3 ± 0.4	14.1 ± 1.4	16.4 ± 1.5	18.7[‡] —
56	18.2 ± 0.1	15.8 ± 0.4	21.0 ± 2.4	19.5 ± 1.2
70	10.5 ± 1.1	9.3 ± 0.5	10.1 ± 2.2	9.5 ± 0.8

[†] Mean quantity from extraction of duplicate subsamples

[¶] Standard deviation

[‡] Lost one subsample

TABLE B-13. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED PERMETHRIN DURING A 25-DAY INCUBATION OF OLIVIER SOIL SUSPENSION AT pH 5.5

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	--- Permethrin, µg/g oven dry solids ---			
1	14.6[†] ± 0.3[¶]	12.0 ± 0.5	15.4 ± 0.3	8.4 ± 0.4
4	15.3 ± 0.8	12.3[‡] —	14.2 ± 0.3	10.9 ± 0.2
6	14.7 ± 0.3	12.6 ± 1.1	11.5 ± 0.2	7.7 ± 2.8
11	12.7 ± 1.0	11.6 ± 0.7	7.6 ± 0.6	6.2 ± 0.0
15	12.2 ± 1.3	11.8 ± 0.6	5.8 ± 0.1	2.3 ± 0.1
18	14.6 ± 0.9	13.0 ± 0.1	8.0 ± 0.1	0.2 ± 0.0
25	11.4 ± 2.5	11.7 ± 1.3	4.2 ± 0.1	0.2 ± 0.1

[†] Mean quantity from extraction of duplicate subsamples

[¶] Standard deviation

[‡] Lost one subsample

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TABLE B-14. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED PERMETHRIN DURING A 26-DAY INCUBATION OF OLIVIER SOIL SUSPENSION AT pH 7.0

Incubation Period, days	Redox Potential, mv -150	50	250	450
	--- Permethrin, μg/g oven dry solids ---			
1	8.7[†] ± 1.8[‡]	16.0 ± 2.5	13.9[¶] —	14.2 ± 0.2
2	10.4 ± 1.1	14.0 ± 1.4	12.4 ± 0.8	12.2 ± 1.9
3	9.7 ± 0.6	10.7 ± 0.3	11.2 ± 0.1	11.8 ± 0.0
5	7.2 ± 1.3	10.7 ± 1.6	9.4 ± 1.1	9.6 ± 1.7
8	6.0 ± 0.3	6.8[¶] —	11.6[¶] —	7.3 ± 0.4
12	8.2 ± 2.4	9.6 ± 0.6	5.5 ± 3.0	4.1 ± 0.5
14	8.2 ± 0.1	9.4 ± 0.6	8.0 ± 0.5	3.2 ± 0.4
19	7.8 ± 0.0	6.9 ± 2.6	5.3 ± 2.6	0.9 ± 0.2
21	7.5 ± 1.1	6.4 ± 1.3	4.6 ± 3.1	0.9 ± 0.0
23	11.1 ± 1.5	11.4 ± 0.8	2.8 ± 2.5	0.6 ± 0.1
26	8.0 ± 0.1	6.8 ± 1.9	1.8 ± 0.1	0.4 ± 0.0

[†] Mean quantity from extraction of duplicate subsamples

[¶] Lost one subsample

[‡] Standard deviation

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TABLE B-15. THE EFFECT OF REDOX POTENTIAL ON THE RECOVERY OF ADDED PERMETHRIN DURING A 26-DAY INCUBATION OF OLIVIER SOIL SUSPENSION AT pH 8.0

Incubation Period, days	Redox Potential, mv			
	-150	50	250	450
	--- Permethrin, µg/g oven dry solids ---			
0	24.0[†] —	17.4[†] —	22.7[†] —	17.4[†] —
2	11.6[¶] ± 0.3[‡]	14.1 ± 1.1	10.7 ± 0.4	12.6 ± 0.1
5	9.1 ± 0.6	8.2 ± 0.2	5.8 ± 1.1	8.2 ± 0.2
12	5.4 ± 1.0	6.5 ± 2.8	1.7 ± 0.3	3.8 ± 0.4
15	6.0 ± 0.7	7.4 ± 1.8	1.5 ± 0.9	2.1 ± 0.1
19	6.9 ± 0.2	5.2 ± 0.1	0.4 ± 0.1	0.4 ± 0.0
23	6.0 ± 0.3	6.1 ± 1.5	0.3 ± 0.0	0.2 ± 0.0
26	6.1 ± 0.4	5.6 ± 1.0	0.3 ± 0.0	0.3 ± 0.0

[†] Lost one subsample

[¶] Mean quantity from extraction of duplicate subsamples

[‡] Standard deviation

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